

Banks, Kendra

219064

From: JOHN CHU [john.chu@uspto.gov]
Sent: Wednesday, March 21, 2007 7:54 PM
To: STIC-EIC1700
Subject: Database Search Request, Serial Number: 10773,366

Requester:
JOHN CHU (P/1752)
Art Unit:
GROUP ART UNIT 1752
Employee Number:
68314
Office Location:
REM 09D51
Phone Number:
(571) 272-1329
Mailbox Number:

SCIENTIFIC REFERENCE BR
Sci & Tech Inf. Cntr.

MAR 22 2007

Pat. & T.M. Office

Case serial number:
10773,366
Class / Subclass(es):
430/157
Earliest Priority Filing Date:

Format preferred for results:
Paper

Search Topic Information:

Please search claim 19 for the azolinyl acetic acid derivative and then its use as a coupler in a heat sensitive recording material.

As background of the chemistry: The diazonium compound couples with the compound of claim 19 upon heating to give an azo dye, thus forming a color.

Thanks you!!

John

Special Instructions and Other Comments:

=> FILE REG

FILE 'REGISTRY' ENTERED AT 18:07:28 ON 28 MAR 2007
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
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=> D HIS

L1 FILE 'LREGISTRY' ENTERED AT 17:47:47 ON 28 MAR 2007
STR

L2 FILE 'REGISTRY' ENTERED AT 17:52:32 ON 28 MAR 2007
40 S L1
L3 659 S L1 FUL
SAV L3 CHU366/A

L4 FILE 'LREGISTRY' ENTERED AT 17:56:47 ON 28 MAR 2007
STR L1

L5 FILE 'REGISTRY' ENTERED AT 17:58:31 ON 28 MAR 2007
1 S L4 SSS SAM SUB=L3
L6 60 S L4 SSS FUL SUB=L3
SAV L6 CHU366A/A

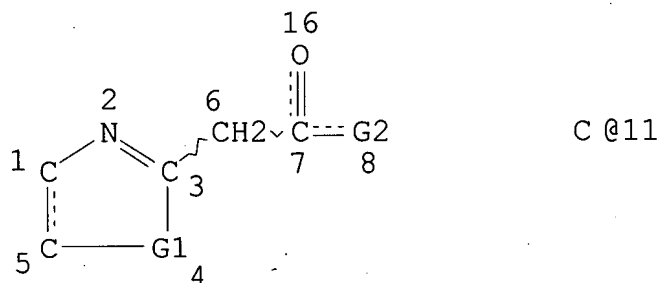
L7 FILE 'CAOLD' ENTERED AT 17:59:21 ON 28 MAR 2007
0 S L6
L8 18 S L3
L9 6884 S ?DIAZO?
L10 0 S L8 AND L9

L11 FILE 'HCA' ENTERED AT 17:59:58 ON 28 MAR 2007
17 S L6
L12 403 S L3
L13 QUE ?DIAZO?
L14 58 S L12 AND L13
L15 751486 S COUPL?
L16 22 S L14 AND L15
L17 9 S L11 AND L16
L18 17 S L17 OR L11
L19 13 S L16 NOT L18
L20 377755 S RECORD?
L21 39927 S (HEAT? OR THERMAL? OR THERMO?) (2A) SENS?
L22 10 S L14 AND L20
L23 2 S L14 AND L21
L24 13 S (L16 OR L22 OR L23) NOT L18
L25 16 S 1840-2004/PY,PRY AND L18
L26 13 S 1840-2004/PY,PRY AND L24

FILE 'REGISTRY' ENTERED AT 18:07:28 ON 28 MAR 2007

=> D L6 QUE STAT

L1 STR



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VAR G2=11/N/O

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NSPEC IS RC AT 11

DEFAULT MLEVEL IS ATOM

DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

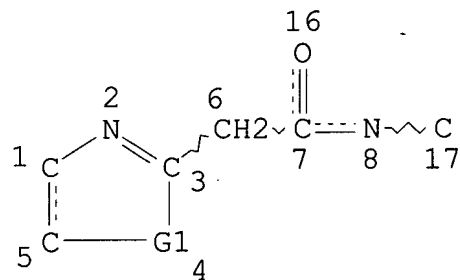
RING(S) ARE ISOLATED OR EMBEDDED

NUMBER OF NODES IS 10

STEREO ATTRIBUTES: NONE

L3 659 SEA FILE=REGISTRY SSS FUL L1

L4 STR



VAR G1=O/S

NODE ATTRIBUTES:

NSPEC IS RC AT 17

DEFAULT MLEVEL IS ATOM

DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RSPEC I

NUMBER OF NODES IS 10

STEREO ATTRIBUTES: NONE

L6 60 SEA FILE=REGISTRY SUB=L3 SSS FUL L4

100.0% PROCESSED 331 ITERATIONS

60 ANSWERS

SEARCH TIME: 00.00.01

=> FILE HCA

FILE 'HCA' ENTERED AT 18:07:50 ON 28 MAR 2007

USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.

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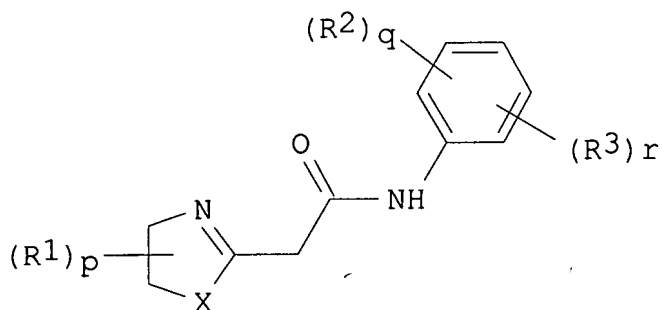
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=> D L25 1-16 CBIB ABS HITSTR HITIND

L25 ANSWER 1 OF 16 HCA COPYRIGHT 2007 ACS on STN

143:430092 Heterocyclic **coupler** compound and its use together with microencapsulated **diazo** compound in **diazo** recording paper. Higuchi, Satoshi; Ikeda, Takayoshi (Fuji Photo Film Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 2005298446 A 20051027, 44 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 2004-120467 20040415.

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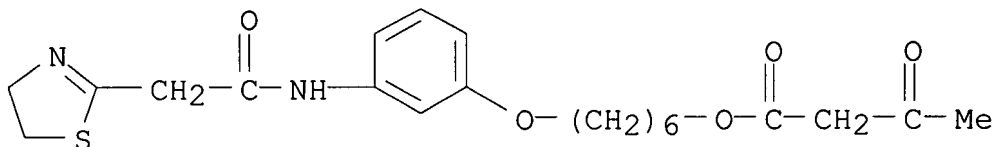
AB The title heterocyclic **coupler** compd. is represented by a general formula I (X = O, S; R1, R2 = substituent; R3 = substituent having 1,3-dicarbonyl structure; p, q = 0-4; r = 1-5). 2 Synthetic examples and 4 **diazo** recording paper examples are given.

IT **868272-22-4 868272-23-5**

(heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)

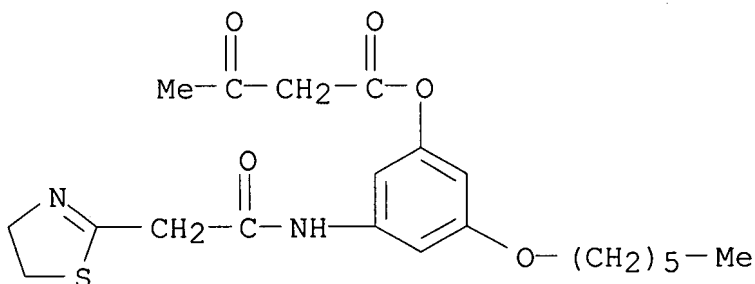
RN 868272-22-4 HCA

CN Butanoic acid, 3-oxo-, 6-[3-[[4,5-dihydro-2-thiazolyl)acetyl]amino]phenoxy]hexyl ester (9CI) (CA INDEX NAME)



RN 868272-23-5 HCA

CN Butanoic acid, 3-oxo-, 3-[[4,5-dihydro-2-thiazolyl)acetyl]amino]-5-(hexyloxy)phenyl ester (9CI) (CA INDEX NAME)

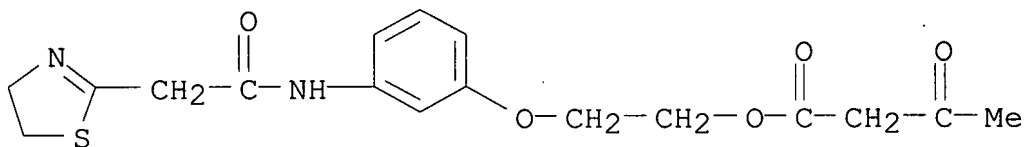


IT **868272-18-8P 868272-21-3P**

(prepn. of heterocyclic **coupler** compd.; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)

RN 868272-18-8 HCA

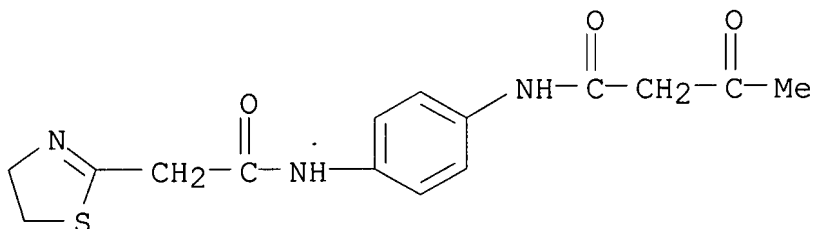
CN Butanoic acid, 3-oxo-, 2-[3-[[4,5-dihydro-2-thiazolyl)acetyl]amino]phenoxy]ethyl ester (9CI) (CA INDEX NAME)



RN 868272-21-3 HCA

CN 2-Thiazoleacetamide, N-[4-[(1,3-dioxobutyl)amino]phenyl]-4,5-dihydro-

(9CI) (CA INDEX NAME)

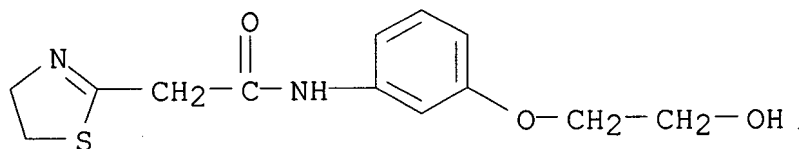


IT 868272-17-7P 868272-19-9P 868272-20-2P

(prepn. of heterocyclic **coupler** compd.; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)

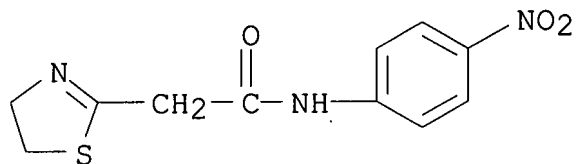
RN 868272-17-7 HCA

CN 2-Thiazoleacetamide, 4,5-dihydro-N-[3-(2-hydroxyethoxy)phenyl]-
(9CI) (CA INDEX NAME)



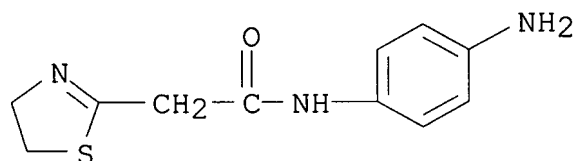
RN 868272-19-9 HCA

CN 2-Thiazoleacetamide, 4,5-dihydro-N-(4-nitrophenyl)- (9CI) (CA INDEX NAME)



RN 868272-20-2 HCA

CN 2-Thiazoleacetamide, N-(4-aminophenyl)-4,5-dihydro- (9CI) (CA INDEX NAME)



- IC ICM C07D277-10
ICS B41M005-28; B41M005-30
- CC 74-10 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)
- ST heterocyclic **coupler** microencapsulated **diazo** compd recording paper
- IT Copying paper
(**diazo**; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
- IT Polyurethanes, uses
(microcapsule; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
- IT **Diazo** process
(paper; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
- IT 663934-47-2
(**diazo** compd.; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
- IT **868272-22-4 868272-23-5**
(heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
- IT 148130-89-6
(microcapsule; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
- IT **868272-18-8P 868272-21-3P**
(prepn. of heterocyclic **coupler** compd.; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
- IT 60-23-1, 2-Aminoethanethiol 100-01-6, 4-Nitroaniline, reactions
372-09-8, Cyano acetic acid 674-82-8, Diketene 16365-26-7,
2-(3-Nitrophenoxy)-ethanol
(prepn. of heterocyclic **coupler** compd.; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
- IT 22208-39-5P 50963-77-4P 128259-54-1P **868272-17-7P**
868272-19-9P 868272-20-2P
(prepn. of heterocyclic **coupler** compd.; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo**

recording paper)

L25 ANSWER 2 OF 16 HCA COPYRIGHT 2007 ACS on STN

143:430091 Heterocyclic **coupler** compound and its use together with microencapsulated **diazo** compound in **diazo** recording paper. Higuchi, Satoshi; Ikeda, Takayoshi (Fuji Photo Film Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 2005298445 A 20051027, 45 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 2004-120466 20040415.

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* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

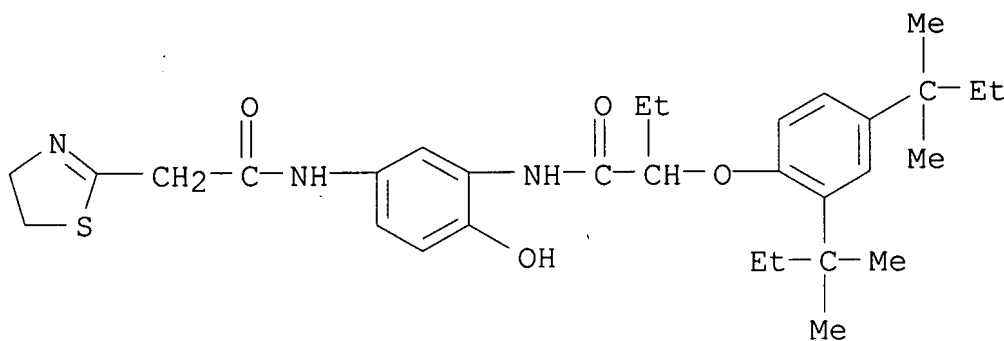
AB The title heterocyclic **coupler** compd. is represented by I or II (X = O, S; R1, R2 = substituent; R3 = acyl, carbamoyl, alkoxy carbonyl, alkylsulfonyl, arylsulfonyl; m = 0-4; n = 0-3; o, p = 0, 1). 4 Synthetic examples and 4 **diazo** recording paper examples are given.

IT **868274-09-3**

(heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)

RN 868274-09-3 HCA

CN 2-Thiazoleacetamide, N-[3-[[2-[2,4-bis(1,1-dimethylpropyl)phenoxy]-1-oxobutyl]amino]-4-hydroxyphenyl]-4,5-dihydro- (9CI) (CA INDEX NAME)

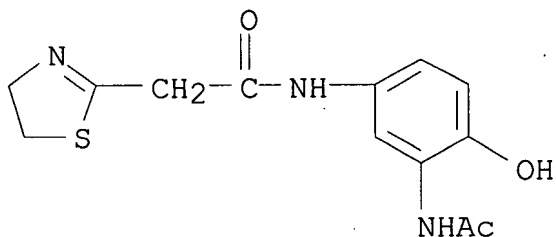


IT **868274-02-6P 868274-04-8P 868274-06-0P 868274-08-2P**

(prepn. of heterocyclic **coupler** compd.; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)

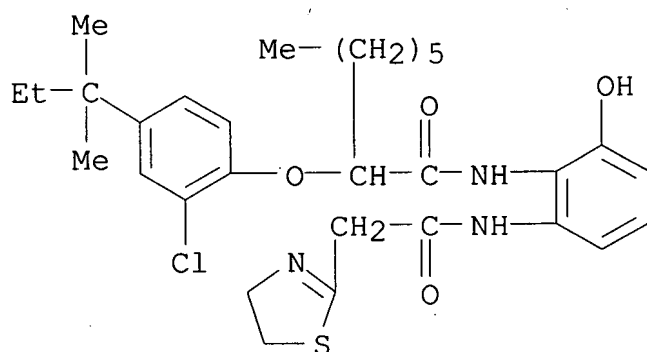
RN 868274-02-6 HCA

CN 2-Thiazoleacetamide, N-[3-(acetylamino)-4-hydroxyphenyl]-4,5-dihydro-
(9CI) (CA INDEX NAME)



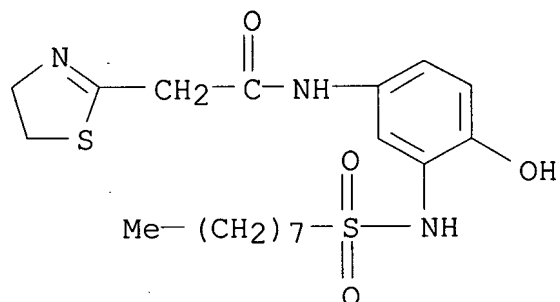
RN 868274-04-8 HCA

CN 2-Thiazoleacetamide, N-[2-[[2-[2-chloro-4-(1,1-dimethylpropyl)phenoxy]-1-oxooctyl]amino]-3-hydroxyphenyl]-4,5-dihydro- (9CI) (CA INDEX NAME)



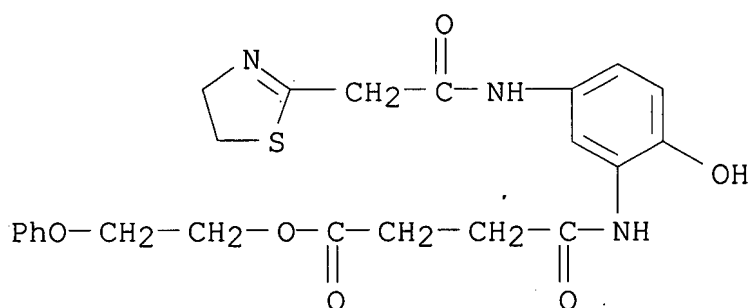
RN 868274-06-0 HCA

CN 2-Thiazoleacetamide, 4,5-dihydro-N-[4-hydroxy-3-[(octylsulfonyl)amino]phenyl]- (9CI) (CA INDEX NAME)



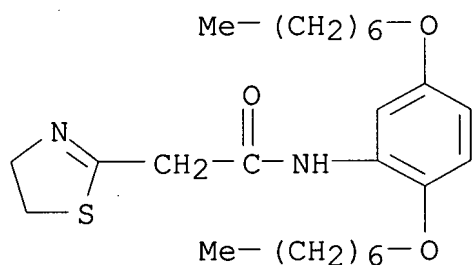
RN 868274-08-2 HCA

CN Butanoic acid, 4-[[5-[[[(4,5-dihydro-2-thiazolyl)acetyl]amino]-2-hydroxyphenyl]amino]-4-oxo-, 2-phenoxyethyl ester (9CI) (CA INDEX NAME)



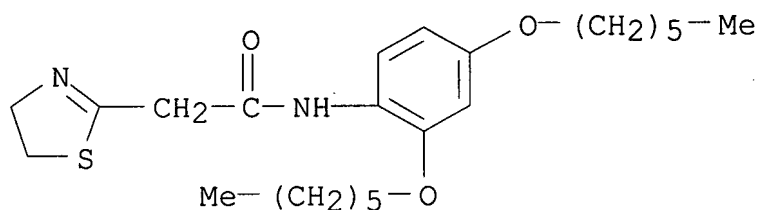
- IC ICM C07D277-10
ICS B41M005-124; B41M005-165; B41M005-28; B41M005-30
CC 74-10 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)
ST heterocyclic **coupler** microencapsulated **diazo** compd recording paper
IT Copying paper
(**diazo**; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
IT Polyurethanes, uses
(microcapsule; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
IT **Diazo** process
(paper; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
IT 663934-47-2
(**diazo** compd.; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
IT **868274-09-3**
(heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
IT 148130-89-6
(microcapsule; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)
IT **868274-02-6P 868274-04-8P 868274-06-0P 868274-08-2P**
(prepn. of heterocyclic **coupler** compd.; heterocyclic **coupler** compd. and its use together with microencapsulated **diazo** compd. in **diazo** recording paper)

- IT 60-23-1, 2-Aminoethanethiol 99-57-0, 2-Amino-4-nitrophenol
 372-09-8, Cyanoacetic acid 868274-03-7 868274-05-9 868274-07-1
 (prepn. of heterocyclic **coupler** compd.; heterocyclic
coupler compd. and its use together with
 microencapsulated **diazo** compd. in **diazo**
 recording paper)
- IT 64-19-7P, Acetic acid, reactions 97-60-9P 23184-60-3P
 868274-01-5P
 (prepn. of heterocyclic **coupler** compd.; heterocyclic
coupler compd. and its use together with
 microencapsulated **diazo** compd. in **diazo**
 recording paper)
- L25 ANSWER 3 OF 16 HCA COPYRIGHT 2007 ACS on STN
 143:413561 Organic base content-controlled heat-developable
diazo recording material with. Ikeda, Kimi (Fuji Photo Film
 Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 2005297378 A
 20051027, 69 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP
 2004-117538 20040413.
- AB The material has a recording layer contg. a **diazo** compd.,
 a **coupler**, and an org. base with pka >5 in less mol
 content than that of the **diazo** compd. The material shows
 improved color development, hue, and less light stain.
- IT **769171-75-7**
 (**coupler**; org. base content-controlled heat-developable
diazo recording material)
- RN 769171-75-7 HCA
 CN 2-Thiazoleacetamide, N-[2,5-bis(heptyloxy)phenyl]-4,5-dihydro- (9CI)
 (CA INDEX NAME)



- IC ICM B41M005-30
 CC 74-10 (Radiation Chemistry, Photochemistry, and Photographic and
 Other Reprographic Processes)
 ST heat developable **diazo** recording material org base
 content; enamine structure **coupler diazo**
 recording material
- IT **Diazo** process
 (heat-developable; org. base content-controlled heat-developable)

- diazo** recording material)
 IT 769171-75-7 867380-72-1 867380-73-2
 (**coupler**; org. base content-controlled heat-developable
diazo recording material)
 IT 67928-21-6 663934-47-2
 (**diazonium** salt; org. base content-controlled
 heat-developable **diazo** recording material)
 IT 101-01-9
 (org. base content-controlled heat-developable **diazo**
 recording material)
- L25 ANSWER 4 OF 16 HCA COPYRIGHT 2007 ACS on STN
 143:356712 Heat-developable **diazo** recording material
 containing protonated dye. Yanagihara, Naoto; Ikeda, Kimi;
 Takeuchi, Yosuke (Fuji Photo Film Co., Ltd., Japan). Jpn. Kokai
 Tokkyo Koho JP 2005271301 A 20051006, 53 pp. (Japanese). CODEN:
 JKXXAF. APPLICATION: JP 2004-85307 20040323.
- AB The material comprises a support coated with a heat-sensitive layer
 contg. protonated dye formed by the reaction of a **diazonium**
 salt and a **coupler**. The material shows good
 lightfastness.
- IT 865619-36-9
 (**coupler**, for yellow dye formation; heat-developable
diazo recording material contg. protonated dye for
 lightfastness)
- RN 865619-36-9 HCA
 CN 2-Thiazoleacetamide, N-[2,4-bis(hexyloxy)phenyl]-4,5-dihydro- (9CI)
 (CA INDEX NAME)

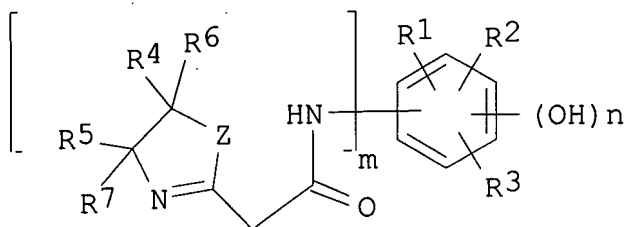


- IC ICM B41M005-30
 ICS B41M005-26
- CC 74-10 (Radiation Chemistry, Photochemistry, and Photographic and
 Other Reprographic Processes)
- ST heat developable **diazo** recording material lightfastness;
 protonated yellow dye **diazonium** salt **coupler**
- IT Microcapsules
 (contg. **diazonium** salt; heat-developable **diazo**
 recording material contg. protonated dye for lightfastness)
- IT **Diazo** process
 (heat-developable; heat-developable **diazo** recording

- material contg. protonated dye for lightfastness)
- IT **865619-36-9** 865619-37-0
(**coupler**, for yellow dye formation; heat-developable **diazo** recording material contg. protonated dye for lightfastness)
- IT 663934-47-2
(**diazonium** salt, yellow; heat-developable **diazo** recording material contg. protonated dye for lightfastness)
- IT 77-99-6D, Trimethylolpropane, reaction products with xylylene diisocyanate 80-05-7D, Bisphenol A, reaction products with xylylene diisocyanate 25854-16-4D, Xylylene diisocyanate, reaction products with trimethylolpropane and/or bisphenol A 266309-16-4, Takenate D 119N
(microcapsule from; heat-developable **diazo** recording material contg. protonated dye for lightfastness)
- IT 865619-38-1
(photoacid generator; heat-developable **diazo** recording material contg. protonated dye for lightfastness)

L25 ANSWER 5 OF 16 HCA COPYRIGHT 2007 ACS on STN
142:326011 Thermal recording material containing **diazo** compound and anilide derivative **coupler**. Arioka, Daisuke; Ikeda, Takayoshi (Fuji Photo Film Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 2005074948 A 20050324, 42 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 2003-311431 20030903.

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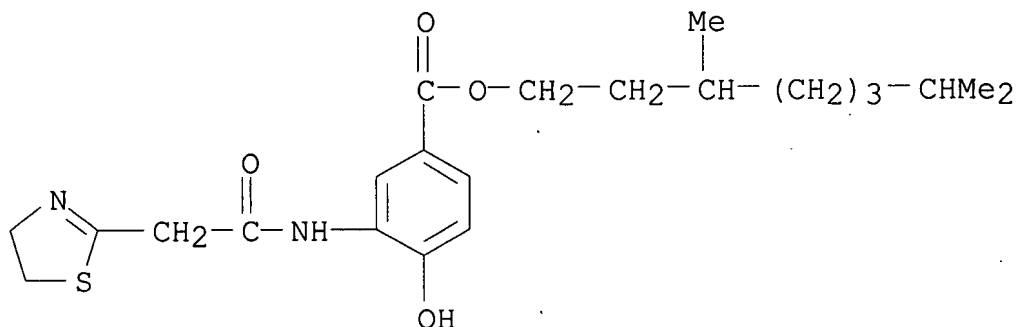
I

- AB The material has a heat-sensitive layer contg. the **diazo** compd. and the **coupler** contg. an anilide deriv. I (R1-3 = H, halo, alkyl, aryl, acyl, alkoxy, aryloxy, alkoxy carbonyl, carboxyl, aminocarbonyl, acylamino, aminosulfonyl, sulfonamide, CN, NO2, arylthio, alkylthio; R4-7 = H, alkyl, aryl, alkoxy carbonyl, amide; Z = S, O, NR8; R8 = H, alkyl, aryl; m = 1, 2; n = 1, 2) and/or its tautomer. The material shows improved raw-stock stability and image stability to light.
- IT **848251-94-5P**
(**coupler**; heat-developable **diazo** recording

material contg. anilide deriv. **coupler**)

RN 848251-94-5 HCA

CN Benzoic acid, 3-[[(4,5-dihydro-2-thiazolyl)acetyl]amino]-4-hydroxy-,
3,7-dimethyloctyl ester (9CI) (CA INDEX NAME)



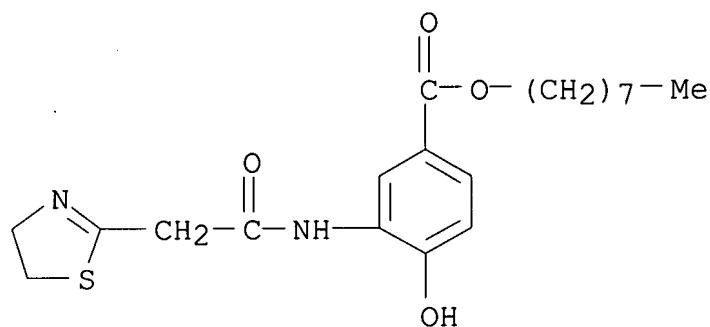
IT **848251-93-4 848251-95-6 848251-96-7**

(**coupler**; heat-developable **diazo** recording

material contg. anilide deriv. **coupler**)

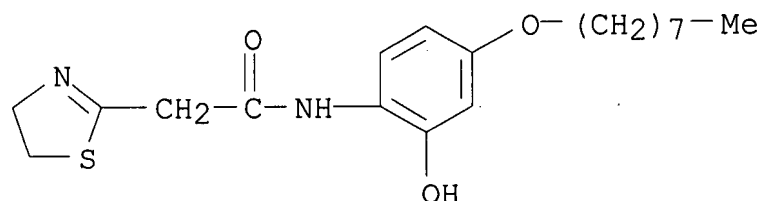
RN 848251-93-4 HCA

CN Benzoic acid, 3-[[(4,5-dihydro-2-thiazolyl)acetyl]amino]-4-hydroxy-,
octyl ester (9CI) (CA INDEX NAME)

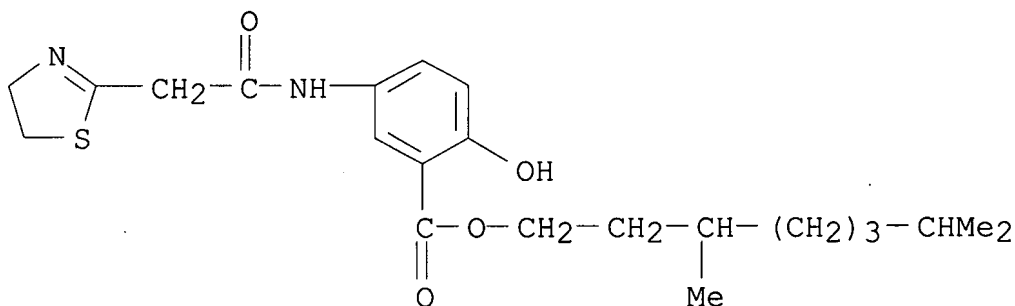


RN 848251-95-6 HCA

CN 2-Thiazoleacetamide, 4,5-dihydro-N-[2-hydroxy-4-(octyloxy)phenyl]-
(9CI) (CA INDEX NAME)



RN 848251-96-7 HCA

CN Benzoic acid, 5-[[(4,5-dihydro-2-thiazolyl)acetyl]amino]-2-hydroxy-,
3,7-dimethyloctyl ester (9CI) (CA INDEX NAME)

IC ICM B41M005-30

ICS B41M005-28

CC 74-10 (Radiation Chemistry, Photochemistry, and Photographic and
Other Reprographic Processes)ST heat developable **diazo** recording anilide **coupler**IT **Diazo** process(heat-developable; heat-developable **diazo** recording
material contg. anilide deriv. **coupler**)

IT Polyureas

Polyurethanes, uses

(microcapsule shell; heat-developable **diazo** recording
material contg. anilide deriv. **coupler**)IT **848251-94-5P**(**coupler**; heat-developable **diazo** recording
material contg. anilide deriv. **coupler**)IT **848251-93-4 848251-95-6 848251-96-7**(**coupler**; heat-developable **diazo** recording
material contg. anilide deriv. **coupler**)

IT 67928-21-6

(**diazo** compd.; heat-developable **diazo**
recording material contg. anilide deriv. **coupler**)

IT 101-01-9

(heat-developable **diazo** recording material contg.
anilide deriv. **coupler**)

IT 96-99-1, 4-Chloro-3-nitrobenzoic acid

(hydrolysis of; prepn. of anilide deriv. **coupler**)

IT 37337-02-3, Takenate D 110N

(microcapsule from; heat-developable **diazo** recording
material contg. anilide deriv. **coupler**)IT 616-82-0P, 4-Hydroxy-3-nitrobenzoic acid 848251-98-9P
848251-99-0P(prepn. of anilide deriv. **coupler**)

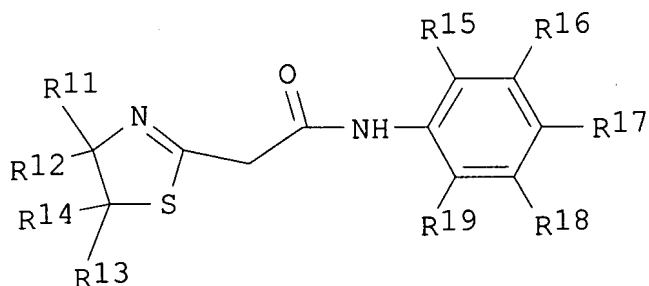
IT 60-23-1, 2-Aminoethanethiol 106-21-8, Tetrahydrogeraniol

372-09-8, Cyanoacetic acid
(prepn. of anilide deriv. **coupler**)

IT 848251-97-8P
(redn. of; prepn. of anilide deriv. **coupler**)

L25 ANSWER 6 OF 16 HCA COPYRIGHT 2007 ACS on STN
142:186610 Heat-developable **diazo** recording material using
specific **coupler**. Higuchi, Satoshi; Arioka, Daisuke;
Ikeda, Takayoshi (Fuji Photo Film Co., Ltd., Japan). Jpn. Kokai
Tokkyo Koho JP 2005028613 A 20050203, 42 pp. (Japanese). CODEN:
JKXXAF. APPLICATION: JP 2003-193339 20030708.

GI



I

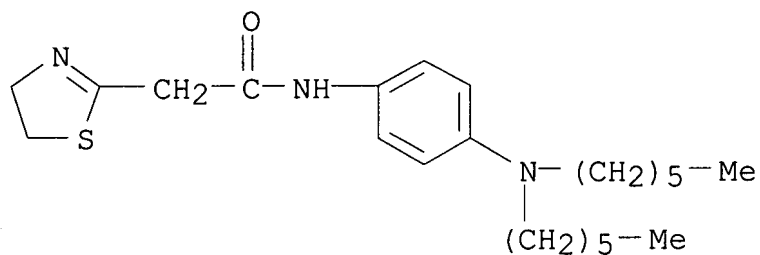
AB The material contains a **diazonium** compd. and a
coupler I [R11-14 = H, alkyl, alkoxy, aryloxy,
alkoxycarbonyl, aryloxycarbonyl, acyloxy, acyl, carbamoyl,
acylamino, sulfamoyl, sulfonamide; R15-19 = H, halo, cyano, alkyl,
aryl, alkoxy, aryloxy, alkylthio, arylthio, alkylsulfonyl,
arylsulfonyl, alkoxycarbonyl, aryloxycarbonyl, acyloxy, acyl,
carbamoyl, acylamino, sulfamoyl, sulfonamide, amino, hydrazino,
hydroxyamino, urea, thiourea; ≥ 1 of R16-18 has Hammett's
 $\sigma_p \leq -0.30$] or its tautomer. The material shows good
storage stability and gives clear yellow images with lightfastness.

IT 833487-25-5 833487-26-6 833487-27-7
833487-28-8 833487-29-9 833487-30-2
833487-31-3

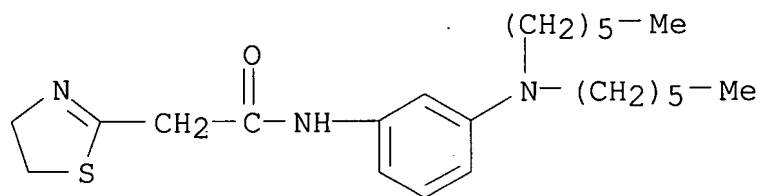
(**coupler**; heat-developable **diazo** recording
material using specific **coupler**)

RN 833487-25-5 HCA

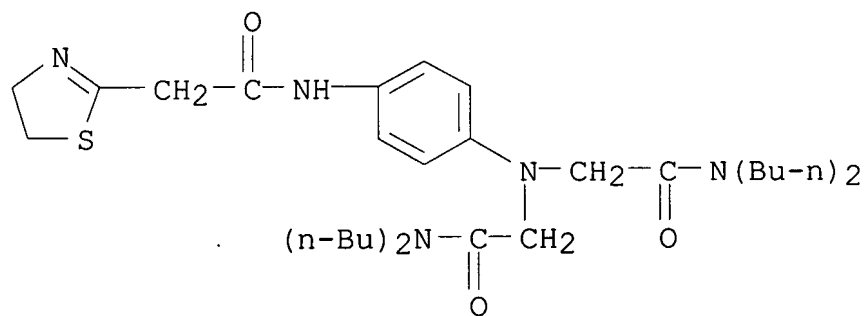
CN 2-Thiazoleacetamide, N-[4-(dihexylamino)phenyl]-4,5-dihydro- (9CI)
(CA INDEX NAME)



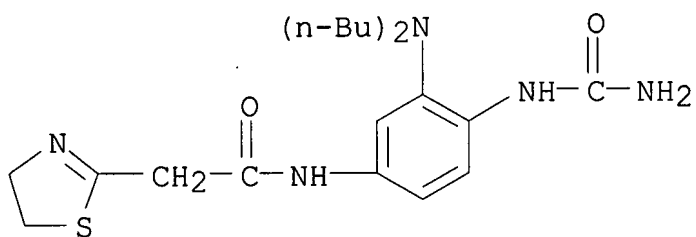
RN 833487-26-6 HCA
 CN 2-Thiazoleacetamide, N-[3-(dihexylamino)phenyl]-4,5-dihydro- (9CI)
 (CA INDEX NAME)



RN 833487-27-7 HCA
 CN 2-Thiazoleacetamide, N-[4-[bis[2-(dibutylamino)-2-oxoethyl]amino]phenyl]-4,5-dihydro- (9CI) (CA INDEX NAME)

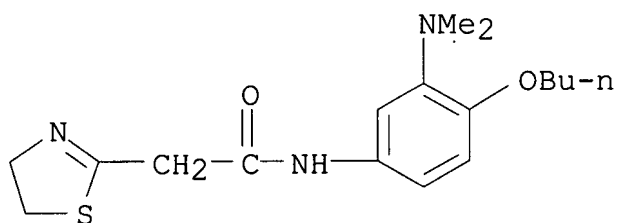


RN 833487-28-8 HCA
 CN 2-Thiazoleacetamide, N-[4-[(aminocarbonyl)amino]-3-(dibutylamino)phenyl]-4,5-dihydro- (9CI) (CA INDEX NAME)



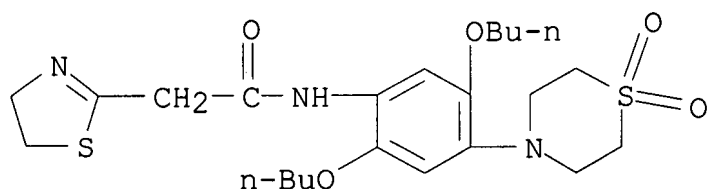
RN 833487-29-9 HCA

CN 2-Thiazoleacetamide, N-[4-butoxy-3-(dimethylamino)phenyl]-4,5-dihydro- (9CI) (CA INDEX NAME)



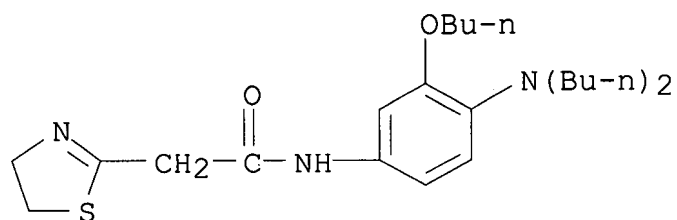
RN 833487-30-2 HCA

CN 2-Thiazoleacetamide, N-[2,5-dibutoxy-4-(1,1-dioxido-4-thiomorpholinyl)phenyl]-4,5-dihydro- (9CI) (CA INDEX NAME)



RN 833487-31-3 HCA

CN 2-Thiazoleacetamide, N-[3-butoxy-4-(dibutylamino)phenyl]-4,5-dihydro- (9CI) (CA INDEX NAME)

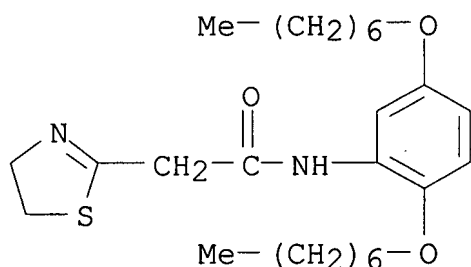


- IC ICM B41M005-30
ICS B41M005-26; B41M005-28
- CC 74-10 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)
- ST heat developable **diazo** recording material yellow
coupler
- IT **Diazo** process
(heat-developable; heat-developable **diazo** recording material using specific **coupler**)
- IT Polyureas
Polyurethanes, uses
(microcapsule shell; heat-developable **diazo** recording material using specific **coupler**)
- IT 833487-25-5 833487-26-6 833487-27-7
833487-28-8 833487-29-9 833487-30-2
833487-31-3
(**coupler**; heat-developable **diazo** recording material using specific **coupler**)
- IT 833487-33-5
(**diazonium** salt; heat-developable **diazo** recording material using specific **coupler**)
- IT 101-01-9
(heat-developable **diazo** recording material using specific **coupler**)
- IT 148130-89-6P
(microcapsule shell; heat-developable **diazo** recording material using specific **coupler**)
- L25 ANSWER 7 OF 16 HCA COPYRIGHT 2007 ACS on STN
141:358159 Heat-developable **diazo** copying materials producing images with good lightfastness. Ikeda, Takayoshi; Saito, Naoki; Kanayama, Shuji (Fuji Photo Film Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 2004291477 A **20041021**, 52 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 2003-88531 20030327.
- AB The materials have copying layers contg. azolinylacetic acids as **couplers** and **diazo** compds. sandwiched between ≥ 2 layers showing O permeability ≤ 20 mL/m²-day. Thus, a material comprising sequential layers of a PET film, an undercoating layer (O permeability 0.01 mL/m²-day), a cyan copying layer contg. **nondiazo** dye, an intermediate layer (O permeability 17 mL/m²-day), a magenta copying layer contg. a **diazonium** compd. and a **coupler**, an intermediate layer (O permeability 24 mL/m²-day), a yellow copying layer contg. a **diazonium** compd. and a **coupler**, a light transmission controlling layer (O permeability 4.3 mL/m²-day), and a protective layer (O permeability 152 mL/m²-day).
- IT **769171-75-7**
(heat-developable **diazo** copying materials using

azolinylacetic acid **couplers** and producing images with good lightfastness)

RN 769171-75-7 HCA

CN 2-Thiazoleacetamide, N-[2,5-bis(heptyloxy)phenyl]-4,5-dihydro- (9CI)
(CA INDEX NAME)



IC ICM B41M005-26

ICS B41M005-28; B41M005-30

CC 74-10 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)

ST heat developable **diazo** azolinylacetic acid **coupler**
; lightfastness heat developable **diazo** copying

IT **Diazo** process

(heat-developable; heat-developable **diazo** copying materials using azolinylacetic acid **couplers** and producing images with good lightfastness)

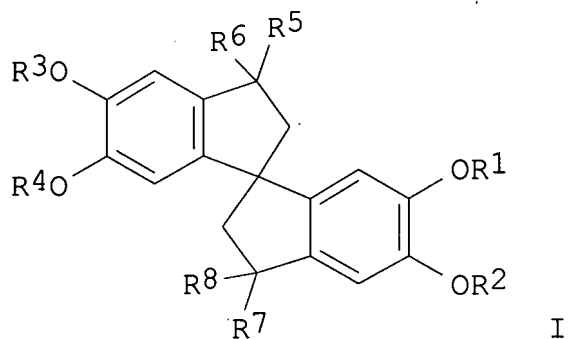
IT 67928-21-6 186612-43-1 460350-61-2 663934-47-2 676461-94-2
769171-75-7

(heat-developable **diazo** copying materials using azolinylacetic acid **couplers** and producing images with good lightfastness)

L25 ANSWER 8 OF 16 HCA COPYRIGHT 2007 ACS on STN

141:322669 Heat-developable **diazo** recording materials. Ikeda, Takayoshi (Fuji Photo Film Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 2004276293 A **20041007**, 52 pp. (Japanese).
CODEN: JKXXAF. APPLICATION: JP 2003-67630 20030313.

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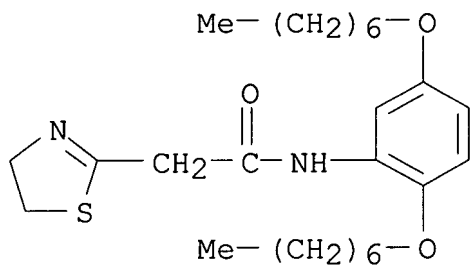
AB The material has a recording layer contg. an azolylacetic acid deriv., a **diazo** compd., and I (R1-4 = alkyl, aryl, heterocycle; R5-8 = H, alkyl, aryl; R5 and R6, and R7 and R8 may form a ring). It shows improved light stability of images.

IT **769171-75-7 769171-78-0**

(**coupler**; heat-developable **diazo** recording material contg. azolylacetic acid **coupler** and spiroindane compd.)

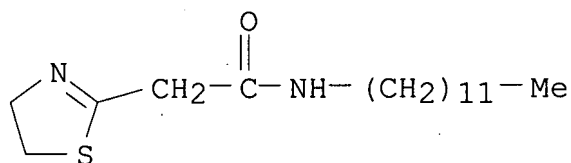
RN 769171-75-7 HCA

CN 2-Thiazoleacetamide, N-[2,5-bis(heptyloxy)phenyl]-4,5-dihydro- (9CI)
(CA INDEX NAME)



RN 769171-78-0 HCA

CN 2-Thiazoleacetamide, N-dodecyl-4,5-dihydro- (9CI) (CA INDEX NAME)



IC ICM B41M005-26

ICS B41M005-28; B41M005-30

CC 74-10 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)

ST heat developable **diazo** recording material spiro indane compd; azolyacetic acid **coupler diazo** recording material

IT **Diazo** process

(heat-developable; heat-developable **diazo** recording material contg. azolyacetic acid **coupler** and spiroindane compd.)

IT **769171-75-7 769171-78-0**

(**coupler**; heat-developable **diazo** recording material contg. azolyacetic acid **coupler** and spiroindane compd.)

IT 67928-21-6 186612-43-1 663934-47-2 676461-94-2

(**diazo** compd.; heat-developable **diazo** recording material contg. azolyacetic acid **coupler** and spiroindane compd.)

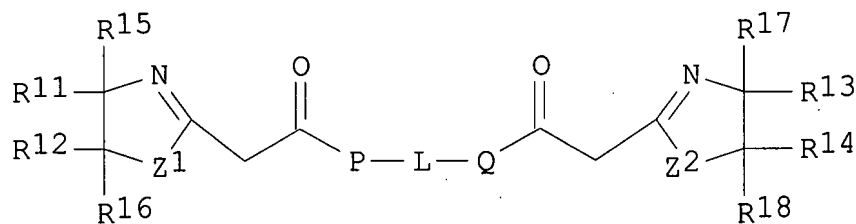
IT 89929-65-7

(heat-developable **diazo** recording material contg. azolyacetic acid **coupler** and spiroindane compd.)

L25 ANSWER 9 OF 16 HCA COPYRIGHT 2007 ACS on STN

141:233287 Novel azonitrile acetate derivative **coupler** and recording material containing the same with improved storage stability. Fujita, Akinori; Saito, Naoki; Takeuchi, Yosuke; Higuchi, Satoshi; Arioka, Daisuke; Ikeda, Takayoshi (Fuji Photo Film Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 2004244316 A **20040902**, 39 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 2003-32491 20030210.

GI



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AB Disclosed is the novel azonitrile acetate deriv. **coupler** which is represented by I (R11-18 = H, alkyl, aryl, etc.; P, Q = single bond, O, amino; L = single bond, divalent org. group; and Z1,2 = S, O, etc.;). Also disclosed is the recording material

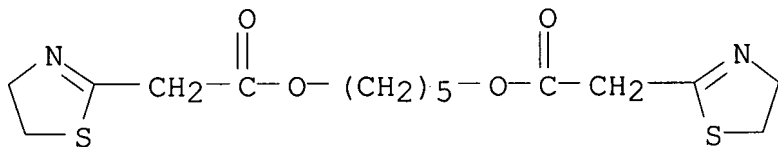
contg. said **coupler** and a **diazonium** salt, in which the **diazonium** salt is encapsulated in a microcapsule.

IT 748795-41-7P 748795-42-8P 748795-43-9P
748795-44-0P

(novel azonitrile acetate deriv. **coupler** for recording material with improved storage stability)

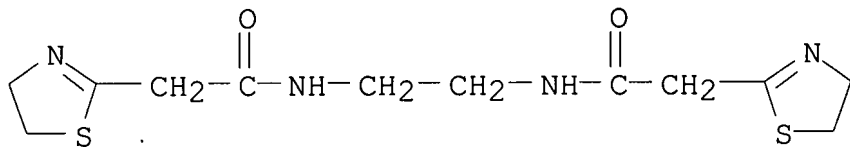
RN 748795-41-7 HCA

CN 2-Thiazoleacetic acid, 4,5-dihydro-, 1,5-pentanediy l ester (9CI)
(CA INDEX NAME)



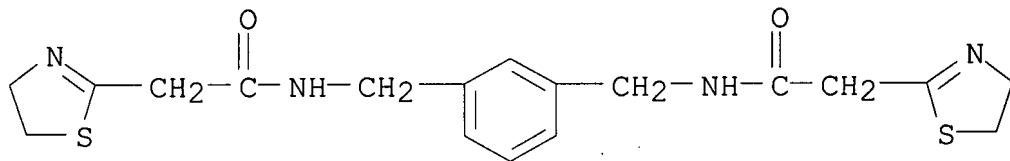
RN 748795-42-8 HCA

CN 2-Thiazoleacetamide, N,N'-1,2-ethanediylbis[4,5-dihydro- (9CI) (CA INDEX NAME)



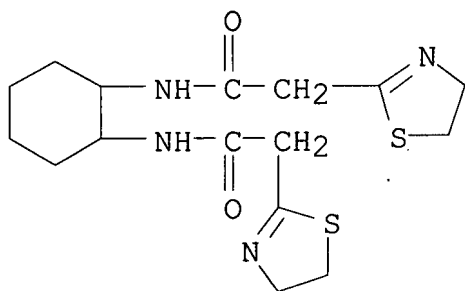
RN 748795-43-9 HCA

CN 2-Thiazoleacetamide, N,N'-[1,3-phenylenebis(methylene)]bis[4,5-dihydro- (9CI) (CA INDEX NAME)



RN 748795-44-0 HCA

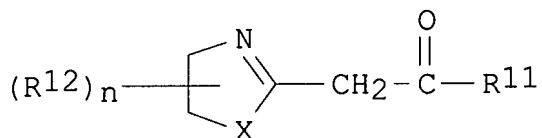
CN 2-Thiazoleacetamide, N,N'-1,2-cyclohexanediylbis[4,5-dihydro- (9CI)
(CA INDEX NAME)



- IC ICM C07D277-10
ICS B41M005-28; B41M005-30; C07D277-82; C07D207-20; C07D211-70;
C07D233-26; C07D263-14; C07D263-56; C07D277-12
- CC 74-10 (Radiation Chemistry, Photochemistry, and Photographic and
Other Reprographic Processes)
Section cross-reference(s): 41
- ST azonitrile acetate deriv **coupler diazonium** salt
recording material
- IT **Diazo** process
(novel azonitrile acetate deriv. **coupler** for recording
material with improved storage stability)
- IT **748795-41-7P 748795-42-8P 748795-43-9P**
748795-44-0P
(novel azonitrile acetate deriv. **coupler** for recording
material with improved storage stability)
- IT 75-75-2, Methanesulfonic acid 105-56-6, Ethyl cyanoacetate
107-15-3, Ethylene diamine, reactions 372-09-8, Cyanoacetic acid
1477-55-0, 1,3-Benzenedimethanamine 29256-90-4, Diaminocyclohexane
(novel azonitrile acetate deriv. **coupler** for recording
material with improved storage stability)

V.9. L25 ANSWER 10 OF 16 HCA COPYRIGHT 2007 ACS on STN
141:197403 Azolinyll acetic acid derivative and azolinyll acetic acid
derivative containing recording material. Saito, Naoki; Matsushita,
Tetsunori; Fujita, Akinori; Takeuchi, Yohsuke; Higuchi, Satoshi;
Ikeda, Kimi (Fuji Photo Film Co., Ltd., Japan). U.S. Pat. Appl.
Publ. US 2004157157 A1 **20040812**, 25 pp. (English).
CODEN: USXXCO. APPLICATION: US 2004-773366 20040209. PRIORITY: JP
2003-32490 20030210.

GI



I

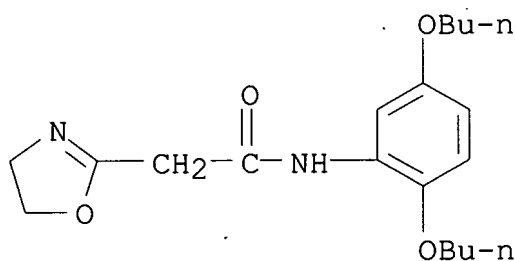
AB The present invention relates to a thermal recording material having, on a support, a recording layer contg. an azolinyl acetic acid deriv. and a diazo compd. The azolinyl acetic acid deriv. is preferably is a compd. represented by formula I (X = O, S; R11 = alkyl group, an aryl group, a heterocyclic group, -OR13 or -NR14R15; R12 = a substituent; R13 = an alkyl group, an aryl group or a heterocyclic group; R14,15 = H, an alkyl group, an aryl group or a heterocyclic group; n = 0-4; and, when n ≥ 2, two or more R12s may be linked with each other to form a ring).

IT **737767-86-1P 737767-87-2P 737767-89-4P**
737767-90-7P

(azolinyl acetic acid deriv. for thermal recording material)

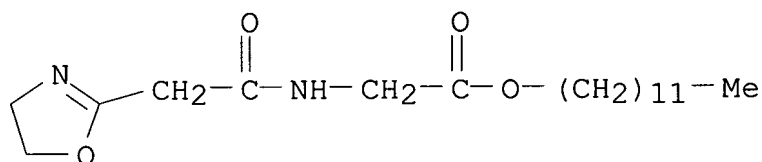
RN 737767-86-1 HCA

CN 2-Oxazoleacetamide, N-(2,5-dibutoxyphenyl)-4,5-dihydro- (9CI) (CA INDEX NAME)



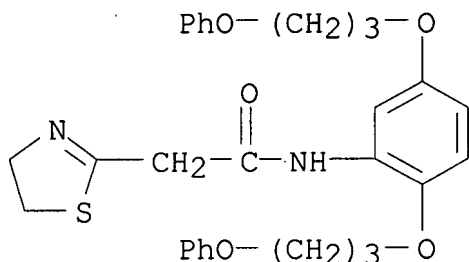
RN 737767-87-2 HCA

CN Glycine, N-[(4,5-dihydro-2-oxazolyl)acetyl]-, dodecyl ester (9CI)
 (CA INDEX NAME)

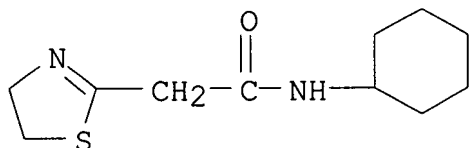


RN 737767-89-4 HCA

CN 2-Thiazoleacetamide, N-[2,5-bis(3-phenoxypropoxy)phenyl]-4,5-dihydro-
(9CI) (CA INDEX NAME)



RN 737767-90-7 HCA
CN 2-Thiazoleacetamide, N-cyclohexyl-4,5-dihydro- (9CI) (CA INDEX NAME)



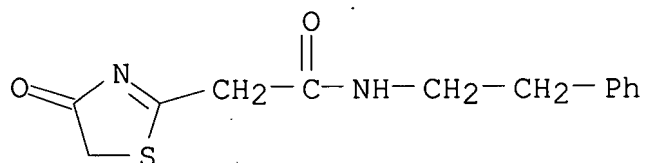
IC ICM G03C001-492
INCL 430270100
CC 74-7 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)
IT **737767-86-1P 737767-87-2P** 737767-88-3P
737767-89-4P 737767-90-7P 737767-91-8P
(azolinyl acetic acid deriv. for thermal recording material)

L25 ANSWER 11 OF 16 HCA COPYRIGHT 2007 ACS on STN
138:254633 Mechanism of stereoselective synthesis of push-pull
(Z)-4-oxothiazolidine derivatives containing an exocyclic double
bond. A MNDO-PM3 study. Markovic, Rade; Vitnik, Zeljko; Baranac,
Marija; Juranic, Ivan (Faculty of Chemistry, University of Belgrade,
Belgrade, 11001, Yugoslavia). Journal of Chemical Research,
Synopsis (10), 485-489 (English) **2002**. CODEN: JRPSDC.
ISSN: 0308-2342. OTHER SOURCES: CASREACT 138:254633. Publisher:
Science Reviews.
AB Calcns. using the MNDO-PM3 method were performed to elucidate the
mechanism of stereoselective base-catalyzed reaction affording
exclusively (Z)-2-alkylidene-4-oxothiazolidine push-pull derivs.
from the corresponding α -mercapto esters and activated
 β -oxonitriles in ethanol as a solvent.
IT **502764-97-8**
(mechanism of stereoselective synthesis of push-pull

(Z)-4-oxothiazolidine derivs. contg. exocyclic double bond and
MNDO-PM3 study)

RN 502764-97-8 HCA

CN 2-Thiazoleacetamide, 4,5-dihydro-4-oxo-N-(2-phenylethyl)- (9CI) (CA
INDEX NAME)



CC 22-2 (Physical Organic Chemistry)

IT 185739-19-9 502764-93-4 502764-94-5 502764-95-6 502764-96-7
502764-97-8 502764-98-9

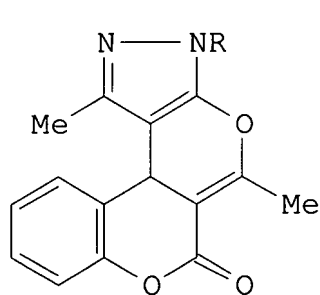
(mechanism of stereoselective synthesis of push-pull

(Z)-4-oxothiazolidine derivs. contg. exocyclic double bond and
MNDO-PM3 study)

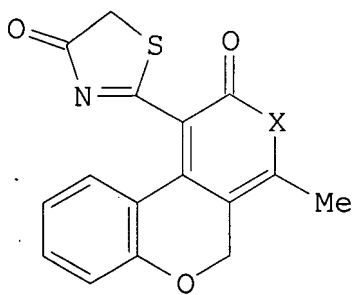
L25 ANSWER 12 OF 16 HCA COPYRIGHT 2007 ACS on STN

118:80855 Reactions with coumarin derivatives: synthesis of several new
coumarinopyrazoles, coumarinopyridines and coumarinyl azoles.
Ismail, Nabila A. (Fac. Sci., Zagazig Univ., Zagazig, Egypt).
Egyptian Journal of Pharmaceutical Sciences, 32(3-4), 685-93
(English) **1991**. CODEN: EJPSBZ. ISSN: 0301-5068.

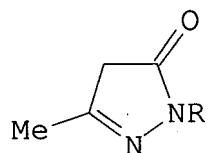
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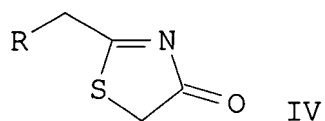
I



II



III



IV

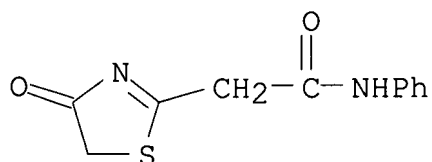
AB New coumarinopyranopyrazoles I (R = H, Ph), and thiazolylcoumarinopyridine II (X = NPh) and -coumarinopyranone II (X = O) were synthesized via the reactions of 3-acetylcoumarin with different active methylene heterocyclic derivs. III (R = H, Ph) and IV (R = CONHPh, CO₂Et) resp. Various other coumarin derivs. were also prepd. by the reactions of 3-(bromoacetyl)coumarin with III and IV (R = CN, CO₂Et, CONHPh).

IT **87007-72-5**

(cyclocondensation of, with acetylcoumarin)

RN 87007-72-5 HCA

CN 2-Thiazoleacetamide, 4,5-dihydro-4-oxo-N-phenyl- (9CI) (CA INDEX NAME)

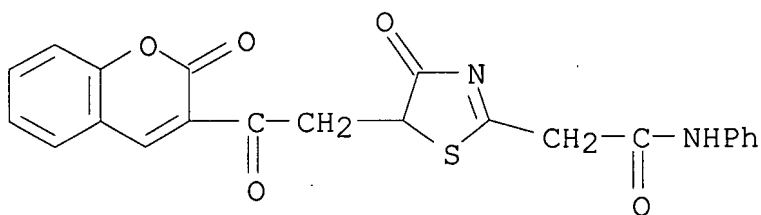


IT **145615-49-2P**

(prepn. of)

RN 145615-49-2 HCA

CN 2-Thiazoleacetamide, 4,5-dihydro-4-oxo-5-[2-oxo-2-(2-oxo-2H-1-benzopyran-3-yl)ethyl]-N-phenyl- (9CI) (CA INDEX NAME)



CC 28-8 (Heterocyclic Compounds (More Than One Hetero Atom))

Section cross-reference(s): 27

IT 89-25-8 108-26-9 877-87-2 **87007-72-5**

(cyclocondensation of, with acetylcoumarin)

IT 145615-41-4P 145615-42-5P 145615-43-6P 145615-44-7P

145615-45-8P 145615-46-9P 145615-47-0P 145615-48-1P

145615-49-2P 145639-99-2P

(prepn. of)

L25 ANSWER 13 OF 16 HCA COPYRIGHT 2007 ACS on STN

116:174042 Heterocycles synthesis through reactions of nucleophiles with acrylonitriles. Part V. Synthesis of several new thiazole and thiazolo[2,3-a]pyridine derivatives. Abdel-Latif, F. F.; Shaker, R.

M. (Fac. Sci., El-Minia Univ., El-Minia, Egypt). Polish Journal of Chemistry, 65(5-6), 1043-8 (English) **1991**. CODEN: PJCHDQ.
ISSN: 0137-5083. OTHER SOURCES: CASREACT 116:174042.

GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

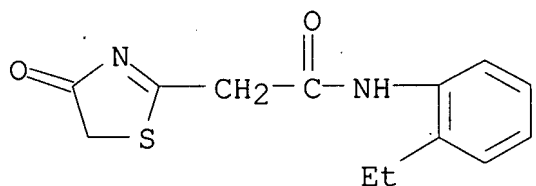
AB RCH:CR1CN (I, R = 2-thienyl, 2-furyl, 1-naphthyl; R1 = cyano) reacted with [(ethylphenyl)carbamoyl]methylthiazolinone II in pyridine to give thiazolopyridines III. In contrast, 2-oxoindolin-3-ylidenemalononitrile and I [R = 2-thienyl, 2-furyl, R1 = C(=O)Ph] reacted with II to give condensation products IV and V, resp. I (R = 2-thienyl, 2-furyl, R1 = CO₂Et) cyclocondensed with II to give dioxotetrahydropyridylthiazolinones VI.

IT **129014-24-0P**

(prepn., condensation, cyclocondensation, and cycloaddn. reaction of, with acrylonitrile derivs.)

RN 129014-24-0 HCA

CN 2-Thiazoleacetamide, N-(2-ethylphenyl)-4,5-dihydro-4-oxo- (9CI) (CA INDEX NAME)



CC 28-7 (Heterocyclic Compounds (More Than One Hetero Atom))

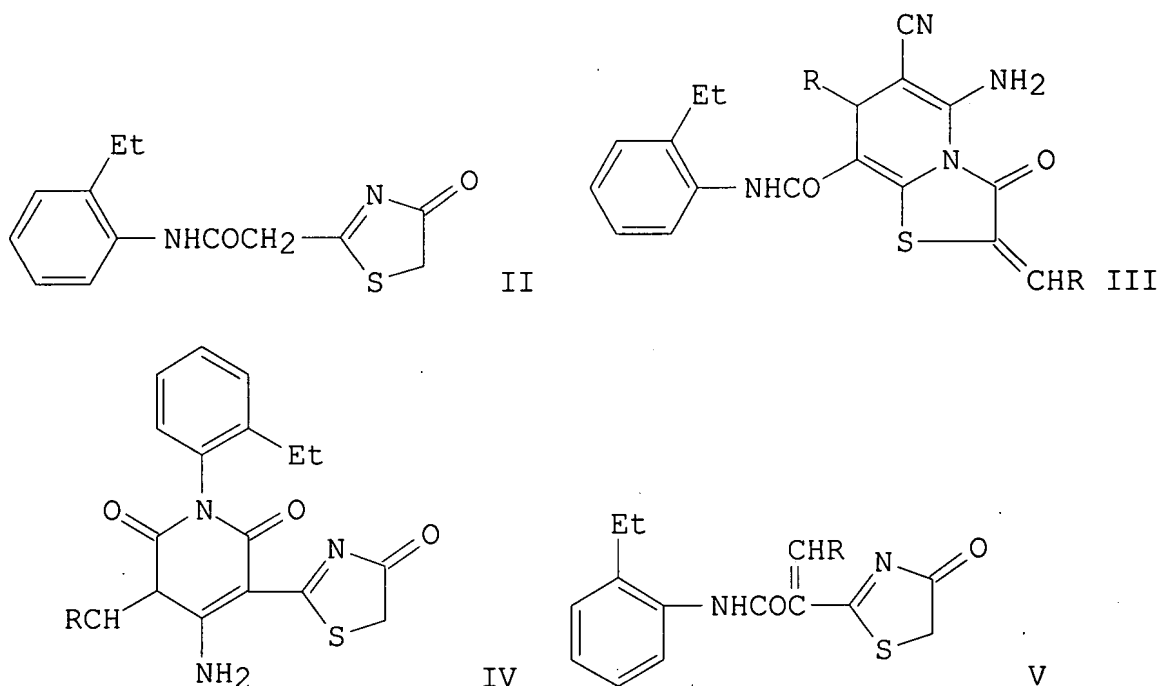
IT **129014-24-0P**

(prepn., condensation, cyclocondensation, and cycloaddn. reaction of, with acrylonitrile derivs.)

L25 ANSWER 14 OF 16 HCA COPYRIGHT 2007 ACS on STN

113:115161 Heterocycle synthesis through reactions of nucleophiles with acrylonitriles. Part 5. Synthesis of several new thiazole and thiazolo[2,3-a]pyridine derivatives. Abdel-Latif, F. F.; Shaker, R. M. (Fac. Sci., El-Minia Univ., El-Minia, Egypt). Phosphorus, Sulfur and Silicon and the Related Elements, 48(1-4), 217-21 (English) **1990**. CODEN: PSSLEC. ISSN: 1042-6507. OTHER SOURCES: CASREACT 113:115161.

GI



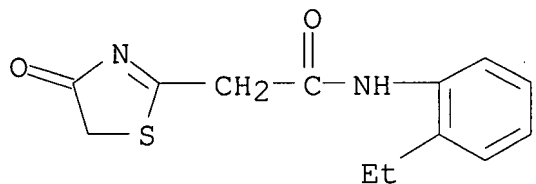
AB Reaction of $RCH:CR_1CN$ (I; $R = 2\text{-thienyl}, 2\text{-furyl}, 1\text{-naphthyl}$; $R_1 = CN$) with thiazolinonylacetylamine II gave thiazolopyridines III. Similar reactions with I ($R = 2\text{-thienyl}, 2\text{-furyl}$; $R_1 = CO_2Et$) gave thiazolinonylpyridinones IV, while with I ($R = 2\text{-indolonyl}, R_1 = CN$; $R = 2\text{-thienyl}, 2\text{-furyl}$; $R_1 = C(=O)Ph$) ylidenes, e.g. V, were obtained.

IT **129014-24-0P**

(prepn. and reactions of, with acrylonitriles, thiazolopyridines, pyridinones, and ylidenes from)

RN 129014-24-0 HCA

CN 2-Thiazoleacetamide, N-(2-ethylphenyl)-4,5-dihydro-4-oxo- (9CI) (CA INDEX NAME)



CC 28-7 (Heterocyclic Compounds (More Than One Hetero Atom))

IT **129014-24-0P**

(prepn. and reactions of, with acrylonitriles, thiazolopyridines, pyridinones, and ylidene derivs. from)

L25 ANSWER 15 OF 16 HCA COPYRIGHT 2007 ACS on STN

110:57610 Activated nitriles in heterocyclic synthesis: a novel synthesis of fused pyrimidine, pyrazole and thiazole derivatives. Ibrahim, Mohamed Kamal Ahmed (Fac. Sci., Cairo Univ., Giza, Egypt). Indian Journal of Chemistry, Section B: Organic Chemistry Including Medicinal Chemistry, 27B(5), 478-81 (English) **1988**. CODEN: IJSBDB. ISSN: 0376-4699. OTHER SOURCES: CASREACT 110:57610.

GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

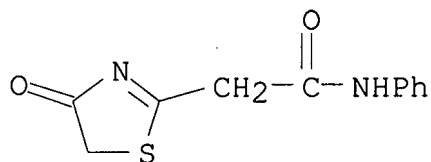
AB Treating p-MeOC₆H₄CH:C(CN)₂ (I) with pyrazolone II (R = H, R₁ = NH₂) gave pyrazolo[1,5-a]pyrimidine III, whereas the treating I with II (R = Cl, R₁ = OH) gave pyrazolo[1,5-b][1,3]oxazine IV. Pyrimido[1,2-a]benzimidazole V was prepd. by treating I with 2-aminobenzimidazole. Treating I with 3-aminotriazole gave s-triazolo[3,4-b]pyrimidine VI. 7H-Thiazolo[3,2-a]pyridine VII was prepd. by treating I with thiazolinone VIII.

IT **87007-72-5**

(reaction of, with anisylidenemalononitrile)

RN 87007-72-5 HCA

CN 2-Thiazoleacetamide, 4,5-dihydro-4-oxo-N-phenyl- (9CI) (CA INDEX NAME)



CC 28-16 (Heterocyclic Compounds (More Than One Hetero Atom))

IT 61-82-5, 1H-1,2,4-Triazol-3-amine 62-56-6, Thiourea, reactions
100-19-6 934-32-7, 2-Aminobenzimidazole 3656-02-8 3656-10-8
87007-72-5 93032-54-3 118464-16-7

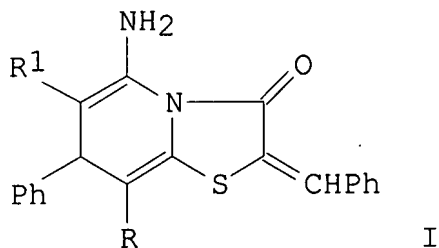
(reaction of, with anisylidenemalononitrile)

L25 ANSWER 16 OF 16 HCA COPYRIGHT 2007 ACS on STN

99:105167 Activated nitriles in heterocyclic synthesis: the reaction of nitriles with mercapto acids. Elgemeie, Galal Eldin Hamza; Elfahham, Hassan Attia; Hassan, Sanna Mohy Eldin; Elnagdi, Mohamed Hilmy (Fac. Sci., Minia Univ., Minia, Egypt). Zeitschrift fuer

Naturforschung, Teil B: Anorganische Chemie, Organische Chemie,
38B(6), 781-5 (English) **1983**. CODEN: ZNBAD2. ISSN:
0340-5087. OTHER SOURCES: CASREACT 99:105167.

GI



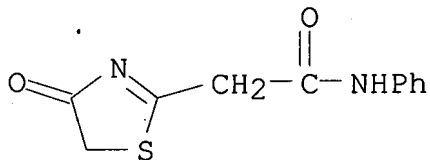
AB New thiazolo[2,3-a]pyridines I (R = cyano, CO₂Et, CONHPh, R₁ = cyano; R = CONHPh, R₁ = CO₂Et) were obtained via the reaction of HSC(:CHPh)CO₂H and HSCH₂CO₂H with some activated nitriles and treatment of the resulting 2-thiazolin-4-ones with PhCH:CR₁CN.

IT **87007-72-5P**

(prepn. and reaction of, with benzylidenemalononitrile)

RN 87007-72-5 HCA

CN 2-Thiazoleacetamide, 4,5-dihydro-4-oxo-N-phenyl- (9CI) (CA INDEX NAME)



CC 28-7 (Heterocyclic Compounds (More Than One Hetero Atom))

IT **87007-72-5P**

(prepn. and reaction of, with benzylidenemalononitrile)

=> D L26 1-13 CBIB ABS HITSTR HITIND

L26 ANSWER 1 OF 13 HCA COPYRIGHT 2007 ACS on STN

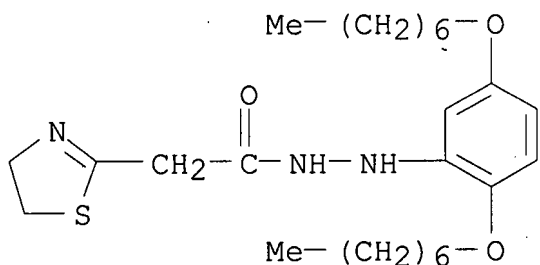
143:68419 **Diazo recording** material containing acylhydrazide **coupler** and **diazo** compound.
Saito, Naoki; Ikeda, Takayoshi (Fuji Photo Film Co., Ltd., Japan).
Jpn. Kokai Tokkyo Koho JP 2005161698 A 20050623, 38 pp.
(Japanese). CODEN: JKXXAF. APPLICATION: JP 2003-404259 20031203.

AB The material has a **recording** layer contg. the acylhydrazide **coupler** and the **diazo** compd. on a support. The material shows improved color developability, raw stock stability, and light stability and reduced background stain.

IT **854089-11-5 854089-13-7 854089-15-9**
854089-17-1 854089-25-1 854089-27-3
 (coupler; diazo recording material
 contg. acylhydrazide **coupler** and **diazo**
 compd.)

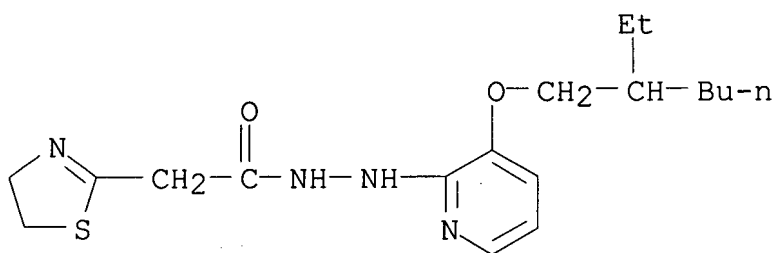
RN 854089-11-5 HCA

CN 2-Thiazoleacetic acid, 4,5-dihydro-, 2-[2,5-bis(heptyloxy)phenyl]hydrazide (9CI) (CA INDEX NAME)



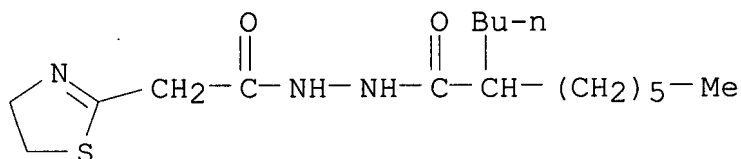
RN 854089-13-7 HCA

CN 2-Thiazoleacetic acid, 4,5-dihydro-, 2-[3-[(2-ethylhexyl)oxy]-2-pyridinyl]hydrazide (9CI) (CA INDEX NAME)

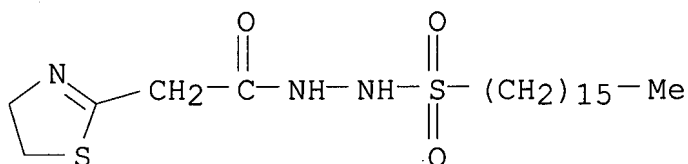


RN 854089-15-9 HCA

CN 2-Thiazoleacetic acid, 4,5-dihydro-, 2-(2-butyl-1-oxooctyl)hydrazide (9CI) (CA INDEX NAME)

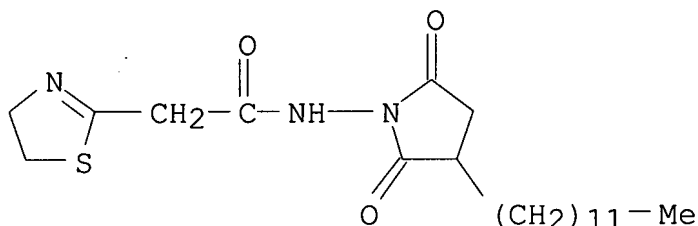


RN 854089-17-1 HCA

CN 2-Thiazoleacetic acid, 4,5-dihydro-, 2-(hexadecylsulfonyl)hydrazide
(9CI) (CA INDEX NAME)

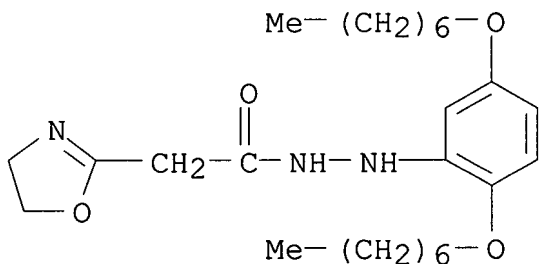
RN 854089-25-1 HCA

CN 2-Thiazoleacetamide, N-(3-dodecyl-2,5-dioxo-1-pyrrolidinyl)-4,5-dihydro- (9CI) (CA INDEX NAME)



RN 854089-27-3 HCA

CN 2-Oxazoleacetic acid, 4,5-dihydro-, 2-[2,5-bis(heptyloxy)phenyl]hydrazide (9CI) (CA INDEX NAME)



IC ICM B41M005-30

ICS B41M005-28

CC 74-10 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)

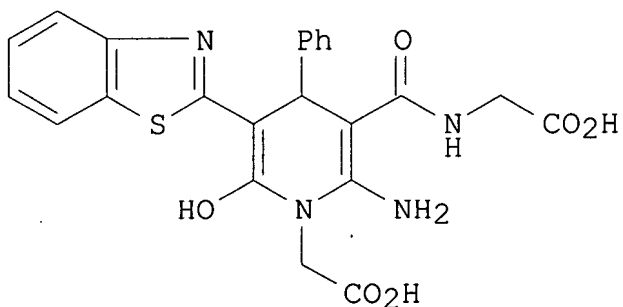
ST **diazo recording** material acyl hydrazide**diazo** compd; heat developable **diazo****recording** materialIT **Diazo** process(heat-developable; **diazo recording** materialcontg. acylhydrazide **coupler** and **diazo**

compd.)
IT 854089-11-5 854089-13-7 854089-15-9
854089-17-1 854089-19-3 854089-21-7 854089-23-9
854089-25-1 854089-27-3 854089-29-5
(coupler; diazo recording material
contg. acylhydrazide coupler and diazo
compd.)
IT 854089-32-0
(diazonium salt; diazo recording
material contg. acylhydrazide coupler and diazo
compd.)

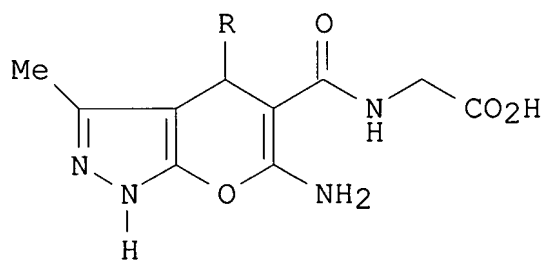
L26 ANSWER 2 OF 13 HCA COPYRIGHT 2007 ACS on STN

132:322108 Amino acid derivatives in organic synthesis, part 4: Facile synthesis of heterocycles containing a glycine residue. Chabaka, Laila M.; Allam, Yehia A.; Nawwar, Galal A. M. (Pesticides Laboratory, National Research Center, Cairo, Egypt). Zeitschrift fuer Naturforschung, B: Chemical Sciences, 55(1), 104-108 (English) 2000. CODEN: ZNBSEN. ISSN: 0932-0776. OTHER SOURCES: CASREACT 132:322108. Publisher: Verlag der Zeitschrift fuer Naturforschung.

GI



I



II

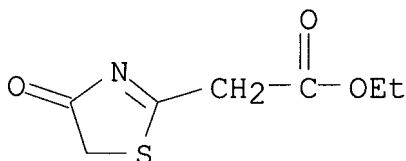
AB Pyridines, thiazolopyridines and pyrazolopyrans contg. glycinate residue, e.g. I and II (R = Ph, 4-chlorophenyl), were prepd. by reacting N-cyanoacryloylglycinate ylidenes with active methylene compds. via a Michael addn. - intracyclization synthetic pathway. Simple routes for the synthesis of heterocycles with an amino acid residue have been previously reported as the incorporation of these residues improves the pharmacokinetics and toxicity of active compds. However, trials to deesterify these residues for **coupling** purposes were unsuccessful. So, we tried herein new approaches for synthesizing heterocycles carrying one or two glycine moieties with free carboxylic acid group to facilitate further peptide linkage on one hand and on the other one could be able to form metal chelates, a property having a significant output on the toxicol. behavior.

IT **877-87-2 29182-42-1**

(prepn. of heterocycles contg. a glycine residue)

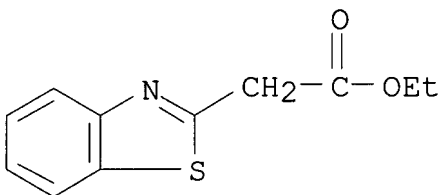
RN 877-87-2 HCA

CN 2-Thiazoleacetic acid, 4,5-dihydro-4-oxo-, ethyl ester (9CI) (CA INDEX NAME)



RN 29182-42-1 HCA

CN 2-Benzothiazoleacetic acid, ethyl ester (8CI, 9CI) (CA INDEX NAME)

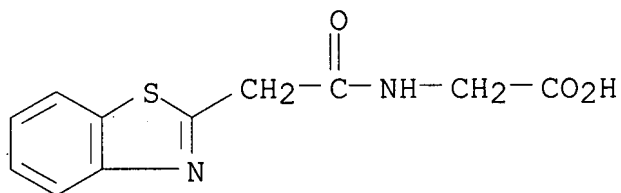


IT **267240-10-8P**

(prepn. of heterocycles contg. a glycine residue)

RN 267240-10-8 HCA

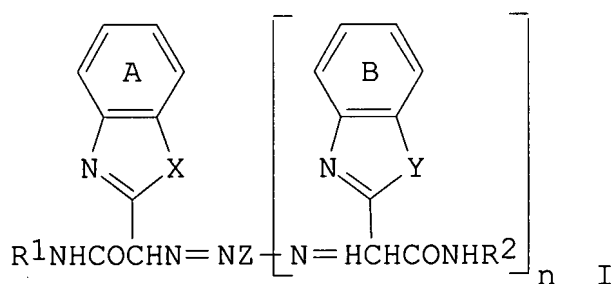
CN Glycine, N-(2-benzothiazolylacetyl)- (9CI) (CA INDEX NAME)



- CC 34-2 (Amino Acids, Peptides, and Proteins)
 Section cross-reference(s): 28
- IT 98-01-1, 2-Furaldehyde, reactions 98-03-3, Thiophene-2-aldehyde
 100-34-5, Phenyl **diazonium** chloride 105-56-6 108-26-9
 109-77-3, Malononitrile **877-87-2** 15743-44-9, Potassium
 glycinate **29182-42-1** 267240-09-5
 (prepn. of heterocycles contg. a glycine residue)
- IT 117580-69-5P 267240-00-6P 267240-07-3P **267240-10-8P**
 267240-11-9P 267240-14-2P
 (prepn. of heterocycles contg. a glycine residue)

L26 ANSWER 3 OF 13 HCA COPYRIGHT 2007 ACS on STN
 116:43076 Azo pigments, their preparation and use. Jung, Ruediger;
 Deubel, Reinhold (Hoechst A.-G., Germany). Ger. Offen. DE 4007535
 A1 **19910912**, 45 pp. (German). CODEN: GWXXBX.
 APPLICATION: DE 1990-4007535 19900309.

GI



AB The pigments (I; R1, R2 = carbocyclic or heterocyclic arom. group;
 X, Y = O, NH, NR3; R3 = aliph. or arom. group; n = 0, 1; Z = arom.
diazo or **bisdiazo** component residue; rings A and B
 may be substituted or annelated) are prepd. by azo **coupling**
 and are suitable for plastics, textiles, and paper. Thus, Et
 2-benzimidazolylacetate was condensed with 2-aminoanisole to give
 the methoxyanilide (II). 4-Chloro-2-nitroaniline was

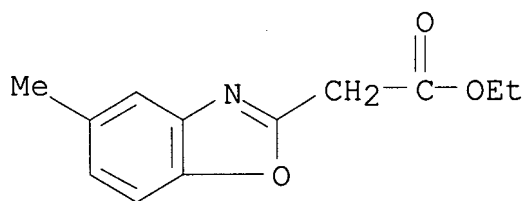
diazotized and **coupled** with II to give reddish yellow I (R1 = o-methoxyphenyl; X = NH; Z = 4-chloro-2-nitrophenyl; n = 0).

IT **138399-44-7P 138420-09-4P**

(prepn. and amidation of)

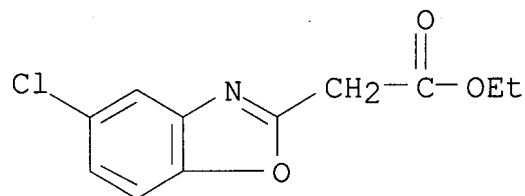
RN 138399-44-7 HCA

CN 2-Benzoxazoleacetic acid, 5-methyl-, ethyl ester (9CI) (CA INDEX NAME)



RN 138420-09-4 HCA

CN 2-Benzoxazoleacetic acid, 5-chloro-, ethyl ester (9CI) (CA INDEX NAME)



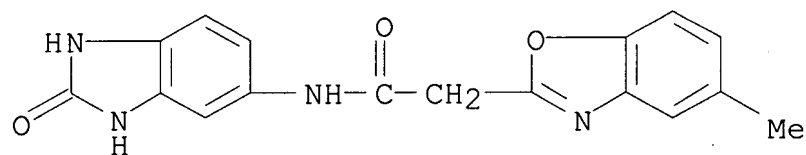
IT **138399-32-3P 138399-39-0P 138399-40-3P**

138399-41-4P 138399-42-5P

(prepn. of, as azo **coupling** component)

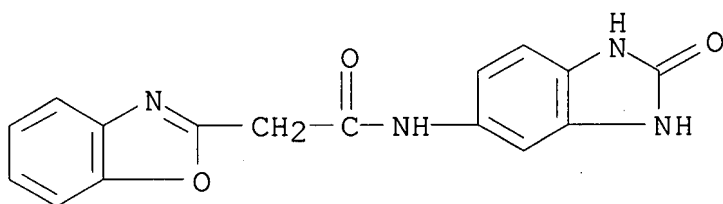
RN 138399-32-3 HCA

CN 2-Benzoxazoleacetamide, N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-5-methyl- (9CI) (CA INDEX NAME)



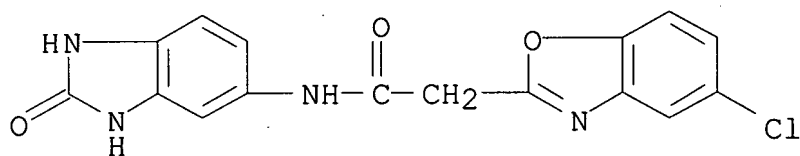
RN 138399-39-0 HCA

CN 2-Benzoxazoleacetamide, N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)- (9CI) (CA INDEX NAME)



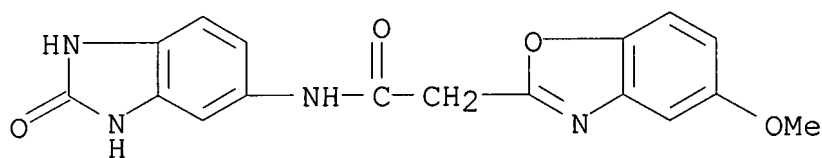
RN 138399-40-3 HCA

CN 2-Benzoxazoleacetamide, 5-chloro-N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)- (9CI) (CA INDEX NAME)



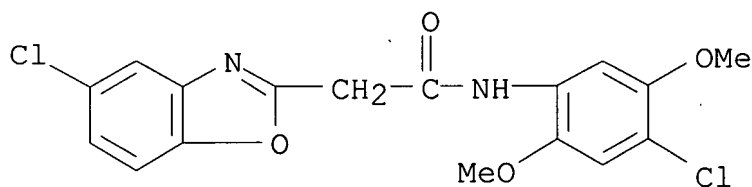
RN 138399-41-4 HCA

CN 2-Benzoxazoleacetamide, N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-5-methoxy- (9CI) (CA INDEX NAME)



RN 138399-42-5 HCA

CN 2-Benzoxazoleacetamide, 5-chloro-N-(4-chloro-2,5-dimethoxyphenyl)- (9CI) (CA INDEX NAME)



IC ICM C09B029-32

ICS C09B035-035; C09B056-12; C09B041-00; C09B063-00; D06P001-44;
C09D017-00; C08K005-34; D01F001-04; B41M001-00

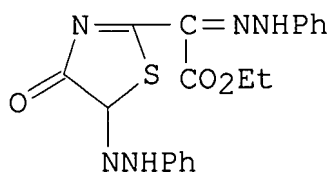
ICA C09D011-02; C09B067-10; C09B067-20; C09B067-22; D06P003-60;
D06P003-40; D06P003-52; D06P003-24; C08K005-3447; C08K005-353

- CC 41-3 (Dyes, Organic Pigments, Fluorescent Brighteners, and Photographic Sensitizers)
- IT 88-17-5, 2-Aminobenzotrifluoride 88-53-9, 2-Amino-5-chloro-4-methylbenzenesulfonic acid 89-62-3, 4-Methyl-2-nitroaniline 89-63-4 95-23-8 95-82-9, 2,5-Dichloroaniline 96-96-8, 4-Methoxy-2-nitroaniline 97-52-9, 2-Methoxy-4-nitroaniline 99-27-4, Dimethyl 5-aminoisophthalate 99-52-5 99-55-8, 2-Methyl-5-nitroaniline 99-59-2, 2-Methoxy-5-nitroaniline 120-35-4, 3-Amino-4-methoxybenzanilide 134-20-3, Methyl 2-aminobenzoate 5372-81-6, Dimethyl aminoterephthalate 19694-10-1, 3-Amino-4-chlorobenzamide 49701-19-1 52298-44-9 67014-36-2 138399-43-6
(**coupling** of **diazotized**, with heterocyclic compds.)
- IT 67499-07-4, 1,2-Bis(2-amino-5-nitrophenoxy)ethane 67499-48-3, 1,2-Bis(4-amino-3-nitrophenoxy)ethane
(**coupling** of tetrazotized, with heterocyclic compd.)
- IT 91-94-1, 3,3'-Dichlorobenzidine 52411-34-4, 1,2-Bis(2-aminophenoxy)ethane
(**coupling** of tetrazotized, with heterocyclic compds.)
- IT 52335-18-9P **138399-44-7P 138420-09-4P**
138420-10-7P
(prepn. and amidation of)
- IT 138399-30-1P 138399-31-2P **138399-32-3P** 138399-33-4P
138399-34-5P 138399-35-6P 138399-36-7P 138399-37-8P
138399-38-9P **138399-39-0P 138399-40-3P**
138399-41-4P 138399-42-5P 138420-07-2P
138420-08-3P
(prepn. of, as azo **coupling** component)

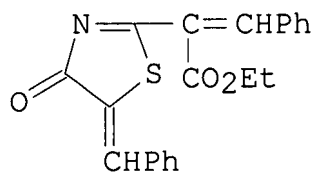
L26 ANSWER 4 OF 13 HCA COPYRIGHT 2007 ACS on STN

112:138951 Reaction of nitriles with mercaptoacetic acid. Facile synthesis of thiazolo[3,2-a]dihydropyridine and thiazolo[4,5-b]pyran derivatives. Ibrahim, Mohamed Kamal Ahmed (Faculty of Science, Cairo Univ., Giza, Egypt). Journal of the Indian Chemical Society, 66(6), 395-7 (English) **1989**. CODEN: JICSAH. ISSN: 0019-4522. OTHER SOURCES: CASREACT 112:138951.

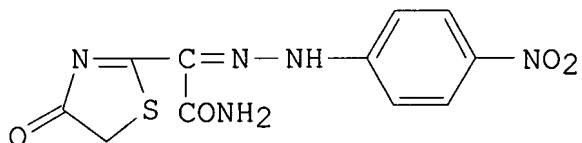
GI



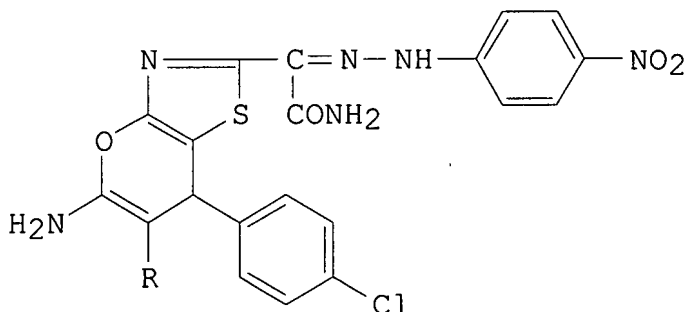
I



II



III



IV

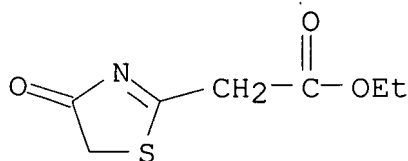
AB 2-Ethoxycarbonylmethyl-4-thiazolinone reacted with 2 equiv each of **benzenediazonium** chloride and benzaldehyde to afford 4-thiazolinone derivs. (I and II, resp.). Treatment of II with malononitrile, cyanoacetamide, Et cyanoacetate, benzoylacetonitrile and cyanoacetanilide gave thiazolo[3,2-a]dihydropyridine derivs. Azocycanoacetamide reacted with mercaptoacetic acid in pyridine to yield 4-thiazolinone III, which was condensed with Et 4-chlorobenzylidenecyanoacetate and 4-chlorobenzylidenemalonitrile to furnish thiazolo[4,5-b]pyran derivs. IV (R = CO₂Et, CN).

IT **877-87-2P**

(prepn. and **coupling** of, with **benzenediazonium** chlorides and benzaldehyde)

RN 877-87-2 HCA

CN 2-Thiazoleacetic acid, 4,5-dihydro-4-oxo-, ethyl ester (9CI) (CA INDEX NAME)



CC 28-7 (Heterocyclic Compounds (More Than One Hetero Atom))

IT **877-87-2P**

(prepn. and **coupling** of, with **benzenediazonium** chlorides and benzaldehyde)

L26 ANSWER 5 OF 13 HCA COPYRIGHT 2007 ACS on STN

110:116632 Synthesis of azo disperse dyes from activated nitriles for dyeing acetate and other fibers. Fadda, A. A.; Elmorsy, S. S.; Elagizy, S. A. (Fac. Sci., Mansoura Univ., Mansoura, Egypt). Indian Journal of Textile Research, 13(2), 87-91 (English) **1988**. CODEN: IJTRDU. ISSN: 0377-8436. OTHER SOURCES: CASREACT 110:116632.

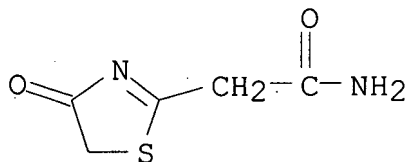
AB 5, α -Bis(aryldiazo)-4-oxo-4,5-dihydro-1,3-thiazol-2-ylacetamides, α -(aryldiazo)cyanoacetic acid hydrazides, and 3-amino-4-(aryldiazo)-2-pyrazolin-5-ones (aryl = C₆H₄R, where R = H, Cl, NO₂, Me, OH, OMe, CO₂H, Br, Cl) were prepd. Azo-hydrazone tautomerism and the effect of the nature and position of the R groups in the **diazonium** components on the color were discussed.

IT **87947-93-1**

(**coupling** of, with **diazotized** aniline derivs.)

RN 87947-93-1 HCA

CN 2-Thiazoleacetamide, 4,5-dihydro-4-oxo- (9CI) (CA INDEX NAME)



CC 41-3 (Dyes, Organic Pigments, Fluorescent Brighteners, and Photographic Sensitizers)

IT 96-96-8

(**coupling** of **diazotized**, with cyanoacethydrazide)

IT 108-44-1, reactions

(**coupling** of **diazotized**, with cyanoacethydrazide)

IT 118-92-3 536-90-3 554-00-7

(**coupling** of **diazotized**, with cyanoacethydrazide or oxodihydrothiazolacetamide)

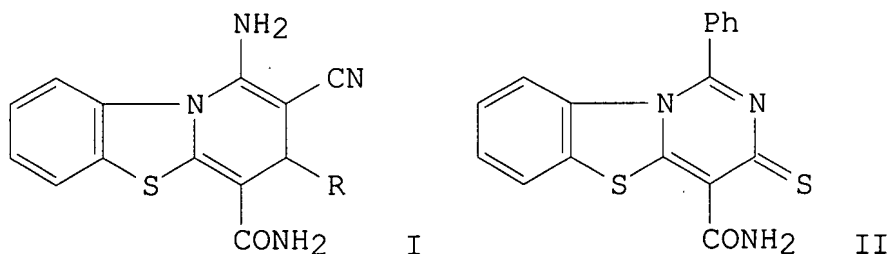
IT 62-53-3, Benzenamine, reactions 88-74-4 95-55-6 100-01-6, reactions 104-94-9 106-40-1 106-47-8, reactions 106-49-0, reactions 108-42-9

(**coupling** of **diazotized**, with cyanoacethydrazide or oxodihydrothiazolacetamide)

IT 140-87-4 **87947-93-1**
(**coupling** of, with **diazotized** aniline
derivs.)

L26 ANSWER 6 OF 13 HCA COPYRIGHT 2007 ACS on STN
109:149468 Studies in sulfur heterocycles: novel synthesis of
pyrido[2,1-b]benzothiazoles and pyrimido[6,1-b]benzothiazoles.
Fathy, Nahed M.; Elgemeie, Galal E. H. (Appl. Org. Chem. Lab., Natl.
Res. Cent., Dokki/Cairo, Egypt). Sulfur Letters, 7(5), 189-96
(English) **1988**. CODEN: SULED2. ISSN: 0278-6117. OTHER
SOURCES: CASREACT 109:149468.

GI

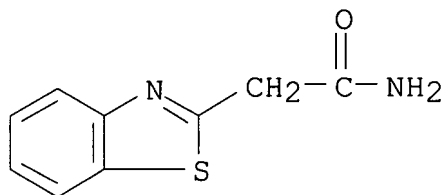


AB A novel synthesis of pyrido[2,1-b]benzothiazoles, e.g., I (R =
4-R₁C₆H₄; R₁ = H, Cl, Me, OMe), and pyrimido[6,1-b]benzothiazoles,
e.g., II, from 2-benzothiazoleacetamide (III) is reported. Thus,
condensation of III with RCHO followed by cyclocondensation with
H₂C(CN)₂ gave I. Direct cyclocondensation of III with RCH:C(CN)₂
gave 56-87% I.

IT **51542-41-7P**, 2-Benzothiazoleacetamide
(prep. and condensation and cyclocondensation reactions of)

RN 51542-41-7 HCA

CN 2-Benzothiazoleacetamide (9CI) (CA INDEX NAME)



CC 28-16 (Heterocyclic Compounds (More Than One Hetero Atom))

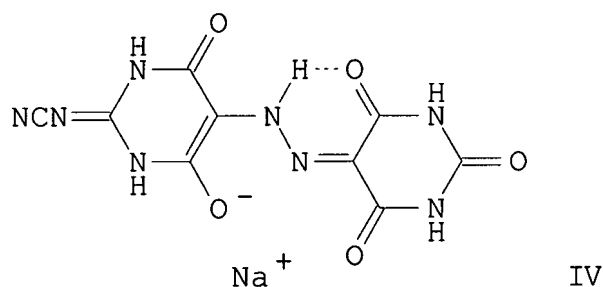
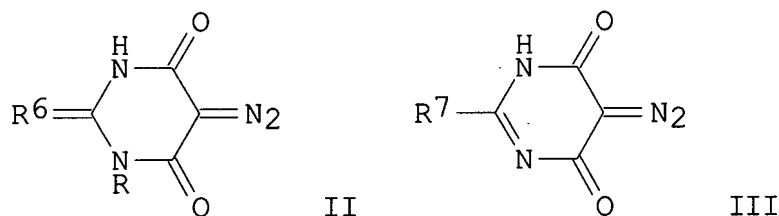
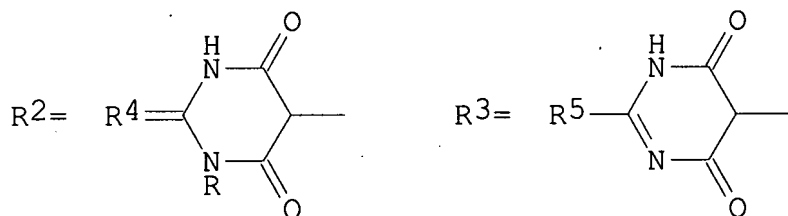
IT **51542-41-7P**, 2-Benzothiazoleacetamide
(prep. and condensation and cyclocondensation reactions of)

IT 62-53-3, Aniline, reactions 104-94-9, 4-Methoxyaniline 106-47-8,

4-Chloroaniline, reactions 106-49-0, 4-Methylaniline, reactions
(sequential **diazotization** and **coupling**
reaction of, with benzothiazoleacetamide)

L26 ANSWER 7 OF 13 HCA COPYRIGHT 2007 ACS on STN
100:69857 Pyrimidine azo pigments. Lorenz, Manfred; Schuendehuette,
Karl Heinz; Bornatsch, Wolfgang (Bayer A.-G., Fed. Rep. Ger.).
Ger. Offen. DE 3307508 A1 **19831103**, 48 pp. (German).
CODEN: GWXXBX. APPLICATION: DE 1983-3307508 19830303. PRIORITY: DE
1982-3215877 19820429.

GI



AB The title azo compds. RN:NR1 (I; $R \neq R1$, $R = R2$ or $R3$ or their tautomers and $R1 =$ **coupling** component residue) were prepd. by **coupling** $R1H$ with II or III, prepd. by resp. reaction of $R2H$ or $R3H$ with $Z(SO_2N_3)_n$ [where $Z =$ alkyl or aryl residue, $n = 1-3$, $R4, R6 = O, N(CN)$, or substituted imino, and $R5, R7 = H$, heterocyclic residue, optionally substituted alkyl, cycloalkyl,

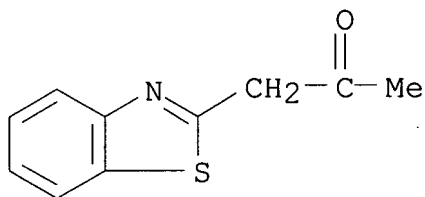
aryl, aralkyl, or amino]. Thus, benzenesulfonyl hydrazide [80-17-1] was treated with HNO₂ to give an emulsion of benzenesulfonyl azide [938-10-3], and barbituric acid [67-52-7] was added to the mixt. to give a suspension of Na **diazobarbiturate** [88638-09-9]. To this suspension 2-cyaniminobarbituric acid [55067-10-2] was added to give Na monocyaniminobarbiturate [88638-10-2] and the suspension was acidified to pH 1 with HCl and heated at 95° to give (IV) [86248-19-3], coloring lacquer and plaster in clear orange shades.

IT **36874-53-0**

(coupling of, with **diazobarbituric acid** deriv.)

RN 36874-53-0 HCA

CN 2-Propanone, 1-(2-benzothiazolyl)- (9CI) (CA INDEX NAME)



IC C09B029-036; C09B041-00

CC 41-3 (Dyes, Organic Pigments, Fluorescent Brighteners, and Photographic Sensitizers)

ST azo pigment pyrimidine; benzenesulfonazide **diazo** pyrimidine; cyaniminobarbiturate azo pigment

IT 67-52-7

(conversion of, to **diazo** derivs.)

IT 88638-09-9

(coupling of, with barbituric acid derivs.)

IT 119-18-6 1076-38-6 14533-64-3

(coupling of, with **diazobarbituric acid**)

IT **36874-53-0** 53815-28-4

(coupling of, with **diazobarbituric acid** deriv.)

IT 88638-11-3

(coupling of, with imino(cyanimino)barbituric acid)

IT 86248-14-8

(coupling of, with **iminodiazobarbituric acid**)

IT 88638-10-2

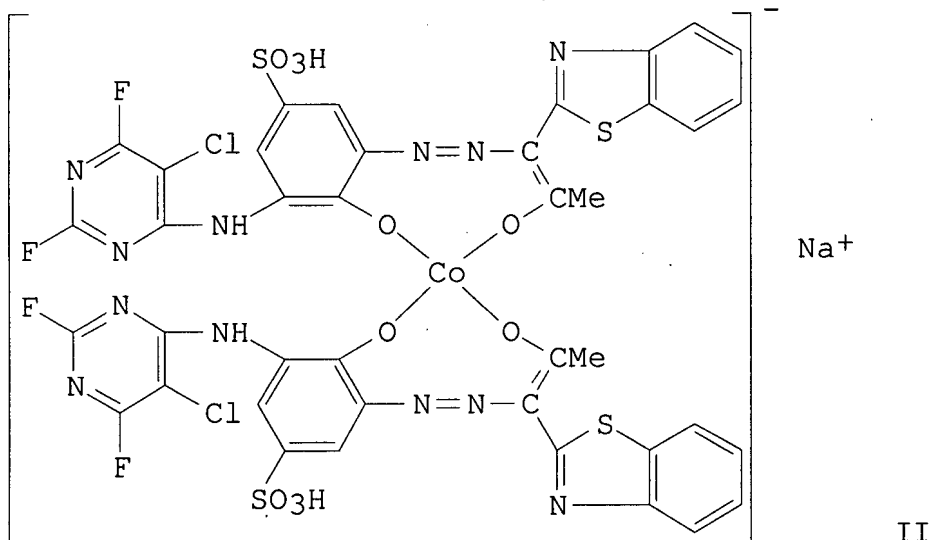
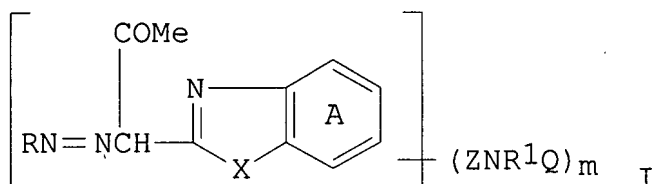
(coupling of, with sodium **diazobarbiturate**)

IT 938-10-3P

(prepn. of, for conversion of barbituric acid derivs. to **diazobarbituric acid** derivs.)

100:53196 Reactive azo dyes. Mennicke, Winfried; Fuerstenwerth, Hauke (Bayer A.-G., Fed. Rep. Ger.). Ger. Offen. DE 3216787 A1 **19831110**, 42 pp. (German). CODEN: GWXXBX. APPLICATION: DE 1982-3216787 19820505.

GI



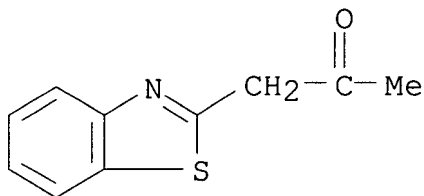
AB Dyes of general structure I (R = **diazo** component residue; X = O, S, NH, substituted NH; Z = direct bond or bridging group; R1 = H, alkyl; Q = fiber-reactive group; m = 1 or 2; ring A may be substituted) and transition metal complexes of I are prepd. I and their complexes are esp. useful as dyes for cotton, polyamide fibers, and wool. Thus, **diazotization** of 2,3,5-HO(AcNH)(HO3S)C6H2NH2 [40306-75-0] and **coupling** with 2-acetylbenzothiazole [**36874-53-0**], deacetylation, complexing with CoCl2, and reaction with 5-chloro-2,4,6-trifluoropyrimidine [697-83-6] gave II [88475-08-5], a light- and wetfast chocolate brown dye for cotton and wool. Yellow, orange, and other brown dyes were also prepd.

IT **36874-53-0**

(**coupling** of, with **diazotized**
(acetamino)aminohydroxybenzenesulfonic acid)

RN 36874-53-0 HCA

CN 2-Propanone, 1-(2-benzothiazolyl)- (9CI) (CA INDEX NAME)



IC C09B062-008; C09B062-012; C09B029-33; D06P001-38

CC 41-3 (Dyes, Organic Pigments, Fluorescent Brighteners, and
Photographic Sensitizers)

IT 6259-63-8 40306-75-0

(**coupling** of **diazotized**, with
acetylbenzothiazole)

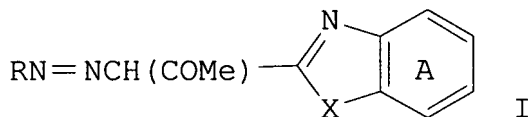
IT **36874-53-0** 88467-77-0

(**coupling** of, with **diazotized**
(acetamino)aminohydroxybenzenesulfonic acid)

L26 ANSWER 9 OF 13 HCA COPYRIGHT 2007 ACS on STN

98:217168 Azo dyes and their metal complex dyes. Mennicke, Winfried;
Fuerstenwerth, Hauke (Bayer A.-G. , Fed. Rep. Ger.). Ger. Offen. DE
3134944 A1 **19830317**, 24 pp. (German). CODEN: GWXXBX.
APPLICATION: DE 1981-3134944 19810903.

GI



AB Monoazo dyes of general structure I and their metal complexes are
prepd., where R represents the residue of a **coupling**
component (preferably a benzeneamine or naphthalenamine with a
complex-forming substituent), X = O, S, or NR1 (R1 = H, alkyl, aryl,
aralkyl, cycloalkyl), and ring A may contain addnl. substituents.
The metal complexes (esp. Co) are fast dyes for amide group-contg.
materials such as leather, wool, and polyamide fibers. Thus,
diazotization of 4,3-HO(H2N)C6H3SO2NH2 [98-32-8] and
coupling with 2-acetylbenzothiazole [**36874-53-0**
] gave I [R = 2,5-HO(H2NSO2)C6H3, X = S] [85935-97-3], which was

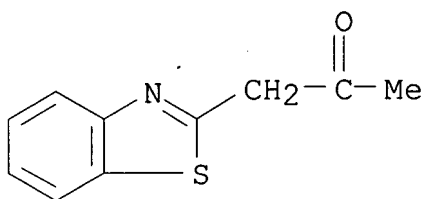
then treated with CoSO₄ in the presence of Na₂CO₃ to form the 1:2 Co complex (II) [83249-73-4]. II, a brown powder, dyed wool, polyamide, and leather in reddish light-brown shades with good fastness to light and wet treatment. Other I and I complexes were similarly prepd.

IT **36874-53-0**

(**coupling** of, with **diazotized**
aminohydroxybenzenesulfonamide)

RN 36874-53-0 HCA

CN 2-Propanone, 1-(2-benzothiazolyl)- (9CI) (CA INDEX NAME)



IC C09B029-32; C09B045-20; D06P001-04; D06P001-10; D06P003-04
CC 41-3 (Dyes, Organic Pigments, Fluorescent Brighteners, and
Photographic Sensitizers)

Section cross-reference(s): 45

IT 96-93-5 98-32-8

(**coupling** of **diazotized**, with
acetonylbenzothiazole)

IT 6635-14-9 **36874-53-0**

(**coupling** of, with **diazotized**
aminohydroxybenzenesulfonamide)

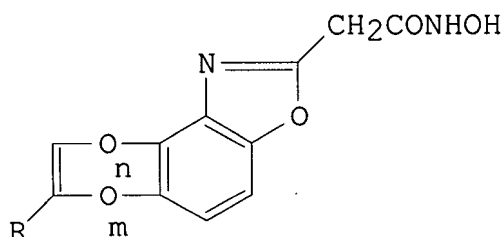
L26 ANSWER 10 OF 13 HCA COPYRIGHT 2007 ACS on STN

88:121156 Furobenzoxazolylacethydroxamic acids. Turin, Michel; Guerret,
Patrick; Pourrias, Bernard; Ruch, Anne Marie (Delalande S. A., Fr.).

Fr. Demande FR 2338041 **19770812**, 16 pp. (French).

CODEN: FRXXBL. APPLICATION: FR 1976-1055 19760116.

GI



I

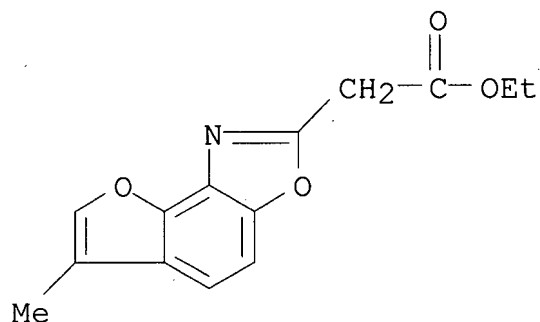
AB The title compds. I ($n = 0, 1$; $m = 1, 0$; $R = C1-4$), bronchodilators, were prepd. Thus, **diazo coupling** of aniline and 2-methyl-5-hydroxybenzofuran followed by $Na_2S_2O_4$ redn. gave 2-methyl-4-amino-5-hydroxy-benzofuran which was cyclocondensed with $EtO_2CCH_2C(:NH)OEt$ and then amidated with $H_2NOH.HCl$ to give I ($R = Me$, $m = 1$, $n = 0$). (II). II gave 46% relaxation in isolated guinea pig trachea.

IT **65874-34-2P**

(prepn. and amidation of, by hydroxylamine)

RN 65874-34-2 HCA

CN Furo[2,3-e]benzoxazole-2-acetic acid, 6-methyl-, ethyl ester (9CI)
(CA INDEX NAME)

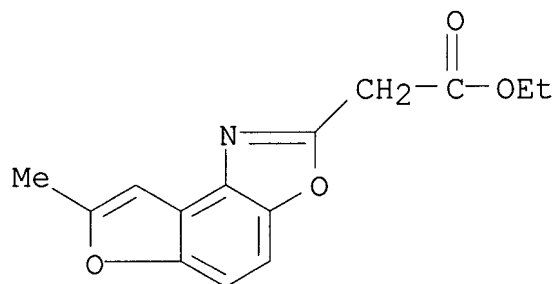


IT **65874-37-5P**

(prepn. and amidation of, by hydroxylamine)

RN 65874-37-5 HCA

CN Furo[3,2-e]benzoxazole-2-acetic acid, 7-methyl-, ethyl ester (9CI)
(CA INDEX NAME)

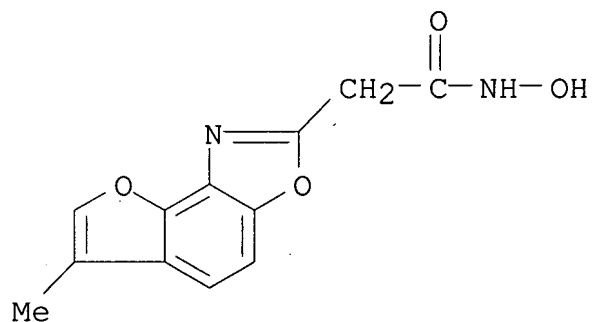


IT **65874-35-3P 65874-38-6P**

(prepn. and bronchodilating activity of)

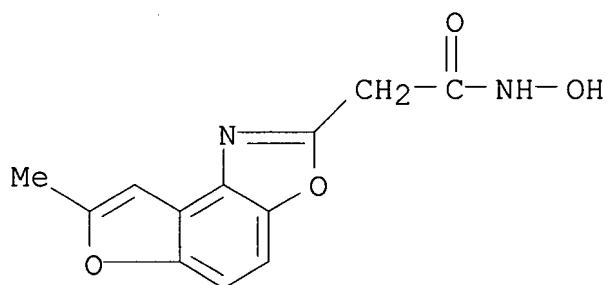
RN 65874-35-3 HCA

CN Furo[2,3-e]benzoxazole-2-acetamide, N-hydroxy-6-methyl- (9CI) (CA
INDEX NAME)



RN 65874-38-6 HCA

CN Furo[3,2-e]benzoxazole-2-acetamide, N-hydroxy-7-methyl- (9CI) (CA INDEX NAME)



IC A61K031-42

CC 28-6 (Heterocyclic Compounds (More Than One Hetero Atom))

IT 6769-56-8

(**coupling** reaction of, with aniline)

IT 62-53-3, reactions

(**coupling** reaction of, with methylhydroxybenzofuran)

IT **65874-34-2P**

(prepn. and amidation of, by hydroxylamine)

IT **65874-37-5P**

(prepn. and amidation of, by hydroxylamine)

IT **65874-35-3P 65874-38-6P**

(prepn. and bronchodilating activity of)

L26 ANSWER 11 OF 13 HCA COPYRIGHT 2007 ACS on STN

80:146965 Azo dyes. Lauer, Dieter; Dehnert, Johannes (BASF A.-G.).

Ger. Offen. DE 2232449 **19740110**, 32 pp. (German). CODEN:

GWXXBX. APPLICATION: DE 1972-2232449 19720701.

AB **Coupling** of **diazotized** RNH₂ (R = substituted phenyl or anthraquinonyl) with 2-(2-benzothiazolyl)acetamides or alkyl (2-benzothiazolyl)acetates gave azo dyes I [R₁ = NH₂, NH(CH₂)₃OMe, NHCH₂CH₂Ph, alkoxy; n = 0 or 1], fast yellow to orange

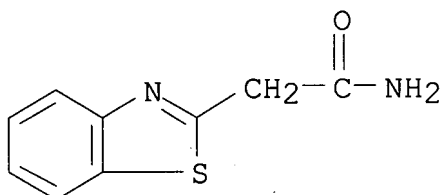
on polyamide (n = 1) and polyester (n = 0) fibers. Thus, 2,4-O₂N(HO₃S)C₆H₃NH₂ was **diazotized** and **coupled** with 2-(2-benzothiazolyl)acetamide [51542-41-7] (prepd. from o-H₂NC₆H₄SH and NCCH₂CONH₂) to give azo dye II [51478-86-5], light-and washfast yellow on polycaprolactam. Similarly, **diazotized** 4,2-Cl(O₂N)C₆H₃NH₂ was. **Coupled** with 2-(2-benzothiazolyl)-N-phenethylacetamide [51478-95-6] to give azo dye I [R = 4,2-Cl(O₂N)C₆H₃, R₁ = NHCH₂CH₂Ph, n = 0] [51478-91-2], fast yellow on polyester fibers. Nine other dyes were prepd.

IT **51542-41-7P**

(prepn. of and **coupling** with **diazotized** aniline derivs.)

RN 51542-41-7 HCA

CN 2-Benzothiazoleacetamide (9CI) (CA INDEX NAME)

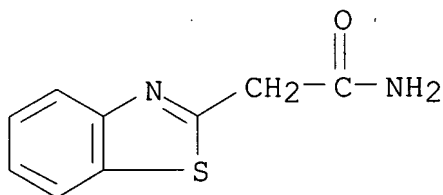


IT **51506-26-4P**

(prepn. of and **coupling** with **diazotized** arom. amines)

RN 51506-26-4 HCA

CN Benzothiazolesulfonic acid, 2-(2-amino-2-oxoethyl)- (9CI) (CA INDEX NAME)



D1-SO₃H

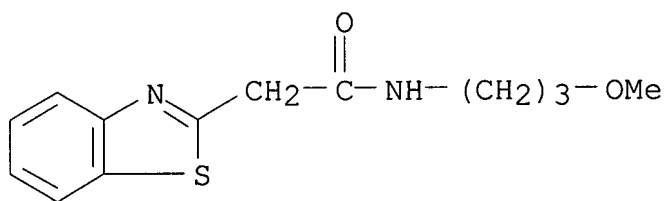
IT **51478-93-4P 51478-95-6P**

(prepn. of and **coupling** with **diazotized** chloronitroaniline)

RN 51478-93-4 HCA

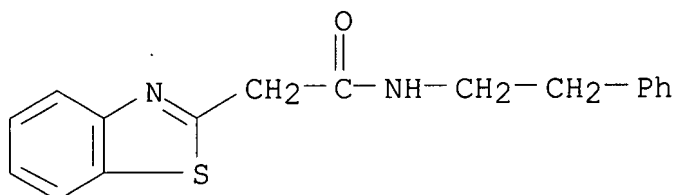
CN 2-Benzothiazoleacetamide, N-(3-methoxypropyl)- (9CI) (CA INDEX

NAME)



RN 51478-95-6 HCA

CN 2-Benzothiazoleacetamide, N-(2-phenylethyl)- (9CI) (CA INDEX NAME)

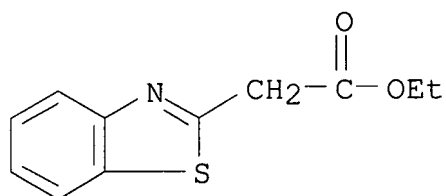


IT 29182-42-1P

(prepn. of and **coupling** with **diazotized**
nitrosulfoaniline)

RN 29182-42-1 HCA

CN 2-Benzothiazoleacetic acid, ethyl ester (8CI, 9CI) (CA INDEX NAME)



IC C09B

CC 40-4 (Dyes, Fluorescent Whitening Agents, and Photosensitizers)

IT 82-45-1 88-74-4 51478-92-3

(**coupling** of **diazotized**, with
(sulfobenzothiazolyl)acetamide)

IT 89-63-4 1817-73-8

(**coupling** of **diazotized**, with
benzothiazolylacetamide)

IT 616-84-2

(**coupling** of **diazotized**, with
benzothiazolylacetic acid derivs.)

IT 51542-41-7P

(prepn. of and **coupling** with **diazotized**

- aniline derivs.)
- IT **51506-26-4P**
(prepn. of and **coupling** with **diazotized** arom.
amines)
- IT **51478-93-4P 51478-95-6P**
(prepn. of and **coupling** with **diazotized**
chloronitroaniline)
- IT **29182-42-1P**
(prepn. of and **coupling** with **diazotized**
nitrosulfoaniline)

L26 ANSWER 12 OF 13 HCA COPYRIGHT 2007 ACS on STN

55:30422 Original Reference No. 55:5971b-i,5972a-c Azo quinone dyes.
Brassel, Jakob; Fasciati, Alfred; Gunst, Raymond; v. Krannichfeldt,
Walter (C I B A Ltd.). US 2938024 **19600524** (Unavailable).
APPLICATION: US .

GI For diagram(s), see printed CA Issue.

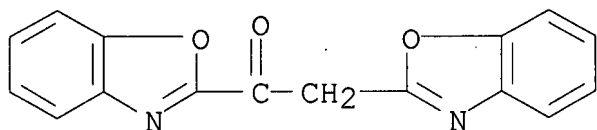
AB A series of dyes of the general formula I was prepd.; in formula I,
n = 1-3, R and R' are benzene radicals, X is an amino bridge bound
to R' meta to the azo linkage, Y represents the radical of a
heterocyclic keto methylene compd. bound to the azo linkage in a
vicinal position to a keto group, Z = H or SO₃H, and A represents a
halogen atom, NH₂, or a radical bound to the C atom directly or
through an O or N bridge. The new dyes are suitable for dyeing or
printing silk, leather, cellulosic, and polyamide and polyurethan
fibers. 1-Amino-4-(p-aminophenylamino)anthraquinone-2-sulfonic acid
(Ia) 8.18 in H₂O 200 contg. NaOH 0.9 and Na₂CO₃ 1.1 treated at
40° with a 25% aq. paste of Na salt of 4,6-dichloro-2-[3-(3-
methyl-5-oxo-2-pyrazolin-4-ylazo)-4-sulfophenylamino]triazine (II)
9.8, stirred 0.5 hr. at 35-40° and 0.5 hr. at 45-50°,
heated to 70°, and filtered, and the residue washed with 2%
aq. NaCl 150 parts yielded a dark powder (III), green in H₂O; it
dyes wool from a neutral or weakly acidic bath clear green tints.
III refluxed 6 hrs. with H₂O 1000 and PhNH₂ 3.8, dild. with satd.
aq. NaCl 120 parts, stirred 15 min., and filtered hot yielded a dark
powder (IV), green in H₂O; it dyes clear green tints. Cyanuric
chloride (V) 18.5 in iced H₂O 400 and 3-methyl-4-(5-amino-2-
sulfophenylazo)-5-pyrazolone (VI) 29.7 [obtained by **coupling**
diazotized 3,4-H₂N(HO₃S)C₆H₃NHAc (VII) with
3-methyl-5-pyrazolone] in H₂O 400 treated dropwise with Na₂CO₃ 10.6
in H₂O 100 parts during 3 hrs. at 2-5° yielded the Na salt of
II. The condensation product 39.3 of V, PhNH₂ and
2,4-(H₂N)2C₆H₃SO₃H (1:1:1 mole) in H₂O 300 and 30% HCl 25
diazotized at about 10-15° with 4N aq. NaNO₂ 25,
treated with NaOAc.3H₂O 30 and then slowly at 10-15° with
1-(o-chlorophenyl)-3-methyl-5-pyrazolone 21.5 in N NaOH 104, and
filtered, the residue stirred with H₂O 1000 at 60°, treated
with Ia 40.9 in H₂O 500 parts at 60°, heated to 90-5°,

neutralized with dil. aq. Na_2CO_3 , cooled to 65° , salted with NaCl , and filtered gave a green powder which produced on wool yellowish green tints. VII 23.0 **diazotized** and **coupled** with 1-(2-methyl-6-chlorophenyl)-3-methyl-5-pyrazolone 20.8, the resulting dye saponified with aq. NaOH at $90-5^\circ$, neutralized at 50° , and filtered, the resulting amino azo dye 45 in H_2O 650 added at $60-70^\circ$ to V 18.4 in ice 200 and H_2O 50 with stirring, stirred 4 hrs. at $10-15^\circ$ while being neutralized with N NaOH , the mixt. treated with a neutralized soln. of Ia 40.9 in H_2O 500, stirred 12 hrs. at 40° while being neutralized with N NaOH , treated with PhNH_2 18.0, stirred 2.5 hrs. at $90-5^\circ$, cooled to 80° , treated with NaCl about 240 parts, stirred, and filtered gave a green dye. The 6- PhNH analog 5.2 of II in H_2O 200 and Ia 4.09 and NaOH 0.4 in H_2O 200 refluxed 24 hrs. while being neutralized with dil. aq. Na_2CO_3 , treated with satd. aq. NaCl 60 parts, and filtered at $50-5^\circ$ gave a dark powder, green, in H_2O ; it dyes clear green tints. V 18.5 in ice 600 and H_2O 200 treated with neutralized 2,4-(H_2N) $2\text{C}_6\text{H}_3\text{SO}_3\text{H}$ 18.8 in H_2O 400 while being kept at pH 6.5 by the continuous addn. of N NaOH 100 parts, kept 15 min. at 0° , adjusted with aq. NaOH to pH 8.5, treated with 4N aq. NaNO_2 25, added during 15 min. into a soln. 60 contg. 30% 1- $\text{Cl}_3\text{H}_7\text{SO}_3\text{H}$, stirred 2 hrs. at 20° , treated with barbituric acid 12.8 in H_2O 400 and 10% aq. Na_2CO_3 200, salted with NaCl , and filtered, the residue in H_2O 1000 treated with di- Na salt of 1-amino-4-(4-amino-3-sulfophenylamino)-2-sulfonic acid (VIII) in H_2O 500 at 60° , stirred 24 hrs. at $40-5^\circ$ at pH 6.5, alkalinized with Na_2CO_3 5 parts, and salted gave a dye which produced on cellulose fibers from an alk. bath contg. a salt, alkali-fast, bluish green tints. The di- Na salt (0.02 mole) of VIII in cold H_2O 400 cc. treated at 0° with V 3.8 g. in Me_2CO 20 cc., stirred 20-30 min. at $0-5^\circ$ while being neutralized with dil. NaOH , neutralized VI 0.02 mole in H_2O 400 cc. added, stirred about 7 hrs. at $35-40^\circ$ while being neutralized continuously with dil. NaOH , and salted gave a dark powder, green in H_2O ; it dyes fast, green shades; it can also be obtained by treating VI 1 with V 1 and then condensing the product with VIII 1 mole. Examples for the dyeing of wool and cotton with some of the dyes are given.

IT **92792-24-0P**, Ketone, 2-benzoxazolyl 2-benzoxazolylmethyl
(prepn. of)

RN 92792-24-0 HCA

CN Ketone, 2-benzoxazolyl 2-benzoxazolylmethyl (6CI, 7CI) (CA INDEX
NAME)



CC 25 (Dyes and Textiles)

IT **92792-24-0P**, Ketone, 2-benzoxazolyl 2-benzoxazolylmethyl
 106322-30-9P, 2-Anthraquinonesulfonic acid, 1-amino-4-[4-[[4-chloro-6-[3-(3-methyl-5-oxo-2-pyrazolin-4-ylazo)-4-sulfoanilino]-s-triazin-2-yl]amino]-3-sulfoanilino]- 106480-97-1P, 2-Anthraquinonesulfonic acid, 1-amino-4-[p-[[4-anilino-6-[3-[1-(6-chloro-o-tolyl)-3-methyl-5-oxo-2-pyrazolin-4-ylazo]-4-sulfonanilino]-s-triazin-2-yl]amino]anilino]- 106570-36-9P, 2-Anthraquinonesulfonic acid, 1-amino-4-[p-[[4-anilino-6-[3-[1-(o-chlorophenyl)-3-methyl-5-oxo-2-pyrazolin-4-ylazo]-4-sulfoanilino]-s-triazin-2-yl]amino]anilino]- 106784-30-9P, 2-Anthraquinonesulfonic acid, 1-amino-4-[p-[[4-anilino-6-[3-(3-methyl-5-oxo-2-pyrazolin-4-ylazo)-4-sulfoanilino]-s-triazin-2-yl]amino]anilino]- 108747-95-1P, p-Benzenedisulfonic acid, 2-[4-[5-[[4-[p-[(4-amino-3-sulfo-1-anthraquinonyl)amino]phenyl]-6-chloro-s-triazin-2-yl]amino]-2-sulfophenylazo]-3-methyl-5-oxo-2-pyrazolin-1-yl]- 109512-17-6P, 2-Anthraquinonesulfonic acid, 1-amino-4-[p-[[4-[3-[1-(o-chlorophenyl)-3-methyl-5-oxo-2-pyrazolin-4-ylazo]-4-sulfoanilino]-6-(cyclohexylmethylamino)-s-triazin-2-yl]amino]anilino]- 117867-09-1P, 2-Anthraquinonesulfonic acid, 1-amino-4-[4-[[4-chloro-6-[3-(hexahydro-2,4,6-trioxo-5-pyrimidinylazo)-4-sulfoanilino]-s-triazin-2-yl]amino]-3-sulfoanilino]- 117879-24-0P, 2-Anthraquinonesulfonic acid, 1-amino-4-[p-[[4-chloro-6-[3-(3-methyl-5-oxo-2-pyrazolin-4-ylazo)-4-sulfoanilino]-s-triazin-2-yl]amino]anilino]- (prepn. of)

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49:15979 Original Reference No. 49:3153h-i,3154a-i,3155a-i,3156a-i,3157a-i,3158a-b Attempted synthesis of penicillins. Bachmann, W. E.; Cronyn, M. W. (Univ. of Michigan, Ann Arbor). Chem. of Penicillin (H. T. Clarke, et al.) (Princeton Univ. Press) 849-91 (Unavailable) **1949**.

GI For diagram(s), see printed CA Issue.

AB In the studies of the synthesis of penicillin, many of the procedures which involved a cyclization in the final step were theor. capable of yielding either the β -lactam or oxazolone-thiazolidine structures. Tests for antibiotic activity were employed as criteria of the potential usefulness of a reaction but no activity greater than 1-2 units per mg. (0.1% activity) was ever obsd. Representative attempts to activate penicilloic acids are reported. In these numerous azlactonizing expts. the agents

used included Ac_2O , Ac_2O in pyridine, acid chlorides, phosphorus trihalides, POCl_3 , PCl_5 , azlactones, and aroyl azides. Various dehydrating agents and adsorbents such as CaCl_2 , CuSO_4 , P_2O_5 , Al_2O_3 , silica gel, Nuchar, etc., were also tried. Control expts. to det. the stability of benzylpenicillin or its β -ester under these operating conditions were performed. Benzylpenicilloic acid, $\text{PhCH}_2\text{CONHCR}(\text{CO}_2\text{H})\text{CH}_2\text{S.CMe}_2\text{CH}(\text{CO}_2\text{H})\text{NH}$ (I, R = H) (Ia) and its esters in the form of racemic mixts. or of optically active isomers and various homologs and analogs were employed. These expts. are classified and tabulated. The few products isolated and characterized proved to be penicillenes formed by cleavage of the thiazolidine ring after azlactonization, the extent of which was detd. by difference from the yield of α -benzylamide. To prevent formation of penicillenes, it was planned to use 6-alkylpenicilloic acid derivs. (I, R = alkyl), but no such compds. were available. Similar blocking attempts by utilizing the benzyl thioamide (instead of the amide) and α -thio ester derivs. of penicilloic acids failed to yield antibiotic active compds. Procedures designed particularly to produce compds. with the β -lactam structure included the action of Grignard reagents on α -alkyl and dialkylpenicilloates. Treatment of benzylpenicilloic acid α -ester with BuMgBr , carbonation, and pyrolysis of the product at $210\text{--}50^\circ$ produced inactive material. Although β -methyl-D- γ -benzylpenicilloate (Ib) treated with PBr_3 in dioxane gave a product with a $5.6\ \mu$ bond in the IR, characteristic of the β -lactam CO group, attempts to isolate the active material by treatment of the mixt. with CH_2N_2 or bases were unsuccessful. Various attempts to form the β -lactam structure by elimination of CO_2 , CO, N, etc., from 5-8 membered rings produced by the closure of suitably substituted penicilloates were unsuccessful, as were efforts based on the elimination of the elements of BzH , NaBr , etc., from similar compds. Prepn. of active compds. was attempted from α -amides, α -hydrazides, and N4-acylpenicilloates. A mixt. of benzylpenicilloic acid α -amide (Ic) (401 mg.) and 156 mg. $\text{BF}_3\cdot\text{Et}_2\text{O}$ complex in 10 mL. dioxane was heated to 100° without sepn. of the $\text{BF}_3\cdot\text{NH}_3$ complex, indicating no reaction. Similarly, cyclization of the HCl salt by heating alone or in solvents could not be accomplished. Attempts to form a triazine and to arrive at the β -lactam by thermal decompn. were made by converting Ic to the α -amido-N-nitroso compd., transformed by treatment with NaOH in dioxane or KOH in MeOH to a compd., m. $133\text{--}4^\circ$, $[\alpha]_{\text{D}}^{23} 16^\circ$ (c 0.49%, EtOH). No antibiotic activity resulted from the thermal treatment of this "triazine" nor was any significantly active material obtained from the product of the nitrosation of the α -hydrazides of the β -esters of benzyl- and phenylpenicilloic acids. Dropwise treatment of 36.6 g. α -Me D-benzylpenicilloate (II) in 50 mL. CHCl_3 contg. 8 mL.

pyridine with 10 mL. Me_2CHCOCl with stirring at room temp. yielded 45 g. α -Me N-isobutyryl-D-benzylpenicilloate; α,β -di-Me ester, m. $123-4^\circ$, hydrolyzed by NaOH in aq. MeOH to the β -Me ester, m. $206-7^\circ$. Formylation of II produced an amorphous N4-formyl deriv. No active material was obtained on pyrolysis of these N4-derivs. Pyrolysis of α -Et β -Me N4-acetyl-N8-methyl-9-phenylpenicilloate gave a compd. with slight antibiotic activity, but none was obtained by the pyrolysis of the monoester or the corresponding N4-isobutyryl compds. The prepn. of benzylpenicillin with the β -lactam structure was attempted by cyclization of di-Me N-carbophenoxy-D-benzylpenicilloate (III) by the Dieckmann procedure. III (125 mg.) in 3 mL. Et₂O and $(\text{ClCH}_2)_2$ was added with stirring to 2 equivs. Me_2CHMgI in 3 mL. Et₂O. Decompn. of the gummy complex with 2N H_2SO_4 gave 80% unchanged III and a small yield of gum which, on sapon. in pyridine, showed no antibiotic activity. Similarly, the di-Me ester of N4-methoxalylbenzylpenicilloic acid failed to cyclize on treatment with NaOMe, Ph_3CNa , BF_3 , or Me_2CHMgBr . Possible prepn. of compds. with the β -lactam structure from cyclization of N-(N-phenylacetyl- β,β -diethoxyalanyl)penicillamine (IV) was early envisaged. In the prepn. of IV, direct formylation of the Et ester of phenaceturylpenicillamine by the action of HCO_2Et and Na was unsuccessful. Addn. of 0.523 g. NaNO_2 in H_2O to 4 g. benzylpenaldic acid di-Et acetal hydrazide in 2N HCl at 0° gave the gummy azide, which was **coupled** with 1.374 g. penicillamine (V) HCl salt by stirring with 0.80 g. Na_2CO_3 and 0.637 g. NaHCO_3 in 15 mL. H_2O 2 h. and recrystg. from aq. EtOH to give colorless needles of IV, m. 67° . Similar condensation of the azide from benzylpenaldic acid di-Me acetal hydrazide, m. 180° with D-V.HCl gave N-(N-phenylacetyl- β,β -dimethoxyalanyl)-D-penicillamine (VI), m. $115-16^\circ$, $[\alpha]_{\text{D}25} 24^\circ$ (c 1.0, MeOH); Me ester, m. 96° , $[\alpha]_{\text{D}25} 36^\circ$ (c 0.1, MeOH). Condensation of the azide from α -phenylacetamide- β,β -dimethoxypropionic acid hydrazide with V Me ester produced a "urea," m. $122-3^\circ$, $[\alpha]_{\text{D}25} -27^\circ$ (c 1.0, MeOH) which evolved H_2S on heating at 100° in Ac₂O to yield an inactive compd., m. $151-2^\circ$. VI showed considerable thermal stability and fusion alone at 150° or with pyridine-HCl at 140° ; these fusions gave material with 0.2-0.5 unit activity per mg. Ring closures of the ester were attempted. Treatment of 2-phenyl-4-ethoxymethylene-5-oxazolone in 2N HCl with abs. EtOH 2 days at room temp. produced N-benzyl- β,β -diethoxyalanine Et ester, m. 48° ; hydrazide (VII), m. $154-5^\circ$, converted by warming at 100° for 1 h. with 2N HCl and EtOH to 2-benzoylamino-3-pyrazolone, m. $200-1^\circ$. Condensation of the azide from VII with V.HCl gave N-(N-benzoyl- β,β -diethoxyalanyl)penicillamine (VIII), m. 150° ; Me ester, m.

90-1°, not cyclized by cold Ac₂O nor by hot pyridine or Ac₂O. Condensation of 20 g. of D-V Me ester-HCl and 22 g. 2-benzyl-4-methoxymethylene-5-oxazolone in 100 mL. pyridine by the addn. of 100 mL. MeOH gave a compd. (IX), m. 140-1°, [α]_D²² 100.7° (c 1.45, MeOH) and N-(α-phenylacetyl-amino-β-methoxyacrylyl)penicillamine Me ester, m. 108.9°, transformed by refluxing with Et₂O to IX, which gave a neg. test for sulfhydryl group, and was hydrogenolyzed over Raney Ni to β-methoxy-N-phenylacetylalanyl-D-valine Me ester, m. 86-7°, identical with a synthetic prepn. Heating IX 2 h. in pyridine at 78-80° or in xylene 16 h. with a trace of Et₂NH gave material with no antibiotic activity. Attempts to effect cyclization of penicillenes with the formation of a thiazolidine ring were fruitless. No antibiotic activity resulted when Me benzyl- or amylpenicillenes were kept in pyridine at room temp. 1 day or on treating the crude penicillenes from the condensation of V and 2-benzyl-4-alkoxy-5-oxazolones with toluene alone or with ascaridole, BzO₂H, N-ethylpiperidine, Ib, or by treatment with pyridine and Cu(OAc)₂. Various attempts to isomerize penillic to penicillenic acids by UV radiation, AlCl₃ in dioxane, Al(Obu-tert)₃ in dioxane, pyridine with ascaridole and with BzO₂H, various acids in (ClCH₂)₂, BF₃, and PhNCO failed to bring about the reversal. Treatment of the oxazole-thiazolidine, N: CPh.O.CCl:CCH.S.CMe₂.CH(CO₂H).NH, with dry pyridine at 60° for 5 h. yielded antibiotically active material (0.25-0.5 units per mg.), quickly inactivated by the action of penicillinase. Condensation of 2-benzyl-4-oxazolecarbonylchloride and V Me ester gave an acylpenicillamine deriv. Portions (3 mL.) of a mixt. of 468 mg. of Me D-5,5-dimethyl-2-thiazoline-4-carboxylate (X) and 444 mg. 2-benzyl-5-oxazolone in 9 mL. toluene were refluxed, and heated at 100° and at 65-70° for 10-min. periods. Samples of the reaction products were saponified and assayed in vitro but showed no activity. No biol. activity was found in products obtained from the condensation of equimolar quantities of 2-phenyl- or 2-amyl-5-ethoxyoxazole with X. To provide a necessary acylaminoketene for reaction with X to produce a compd. with β-lactam structure, 2.64 mL. PhCH₂COCl was added to a suspension of Hg₂(NCO)₂ in 15 mL. dry benzene and the filtered soln. was satd. with dry HCl to give presumably PhCH₂CONHCOCl, m. 105-8° (phenylacetylurea, m. 209-10°). Treatment with excess CH₂N₂ gave presumably PhCH₂CONHCOCHN₂, which was rearranged with Ag₂O to PhCH₂CONHCHC:O in the presence of X to yield biol. active but not reproducible products. A large no. of investigations were concerned with the prepn. of "dehydropenicillins" of the structure N:C(CH₂Ph).O.CO.CHC:N.CH(CO₂H).CMe₂.S, or N:C(CH₂Ph).O.CO.C:C.NH.CH(CO₂H).CMe₂.S (XI), which would give the oxazolone-thiazoline structure on redn. Refluxing 15 g. NaH₄.H₂O with 20.7 g. PhCH₂CONHCH₂CO₂Me in 50 mL. MeOH 1 h. and recrystg. the

product from Me₂CHOH yielded phenaceturyl hydrazide, m. 130-2°, converted to the azide, m. 85-6°, which was condensed with V.HCl to crude D-N-phenaceturylpenicillamine, m. 137-40°. Cyclization by standing for 5 days in satd. ethereal HCl gave a product whose anal. corresponded to that of dehydrobenzylpenilloic acid-HCl (XII). Simultaneous addn. of 125 g. PhCH₂COCl and 32 g. NaOH in H₂O below 0° to 100 g. of H₂NCH₂CN.H₂SO₄ in 500 mL. H₂O contg. 52 g. NaOH yielded 70 g. phenylacetamidocetonitrile, m. 93, converted by treatment with dry HCl at 0° in dioxane and MeOH to phenylacetamidacetimino Me ether-HCl, m. 158° (Et ether-HCl, m. 165°), yielding with excess Na₂CO₃ in Et₂O the corresponding ethers (Me, m. 80-1°; Et, m. 91-2.5°). Condensation of either of these ethers with V Me ester-HCl gave XII Me ester, b_{0.1} 180-90°, reduced in Et₂O over Al-Hg to Me benzylpenilloate (HCl salt, m. 85-95°), cleaved by HgCl₂ to benzylpenilloaldehyde, identified by the 2,4-dinitrophenylhydrazone, m. 195-8°. A mixt. of 1.8 g. H₂NCH(CO₂Et)₂ in 25 mL. Et₂O and 1.5 g. Na₂CO₃ in 10 mL. H₂O was shaken and 1.5 g. PhCH₂COCl was added dropwise; warming to complete reaction and sepg. the Et₂O layer gave di-Et phenylacetamidomalonate, m. 67-8°. Treatment of 1.08 g. of this ester in 5 mL. EtOH contg. 0.21 g. KOH, evapn. to dryness, soln. in H₂O, acidification and recrystn. from CHCl₃-petr. ether produced mono-Et phenylacetamidomalonate, m. 104-5°. This half-ester was converted to the hydrazide, m. 143-5°, and then to the colorless cryst. azide, which was filtered off and added to V.HCl in aq. Na₂CO₃. After 15 min. the mixt. was acidified with HCl to yield N-(N-phenylacetyl-α-carboxyglycyl)penicillamine, m. 152-3°. The compd. appeared to react with ethereal HCl but no cryst. products were isolated. Similarly, the monoazide of benzoylaminomalononic acid was **coupled** with V and its Me ester without prodn. of cryst. material. No definite products were obtained from N-phenaceturylpenicillamine Me ester and CH(OEt)₃, HCSNH₂ or CHCl₃. Another approach employed 2-benzyl-4-carbethoxy-5-oxazolone (XIII). Phenylacetamidomalononic acid ester hemihydrate (1 g.) was warmed on the steam bath 30 min. with 10 mL. Ac₂O, freed from excess reagent in vacuo, and distd. in vacuo at 50-60° gave PhCH₂CONHCH₂CO₂Et, m. 79-80°. XIII reacted readily with PhNH₂ and p-H₂NC₆H₄Me to produce phenylacetamidomalonanilic Et ester, m. 156°, and the corresponding toluidide Et ester, m. 157-8°. Addn. of 1 g. crude XIII to 500 mg. of cysteine Me ester in 15 mL. benzene and 5 mL. AcOEt and recovery of the residue from Et₂O gave N-(N-phenylacetyl-α-carbethoxyglycyl)cysteine Me ester, m. 106-20°. Similarly, allowing a mixt. of XIII and V Me ester to stand in Et₂O overnight, extg. with 2N HCl and aq. Na₂CO₃, concg. the Et₂O ext. and recrystg. the residue from CHCl₃-petr. ether gave N-(N-phenylacetyl-α-

carbethoxyglycyl)penicillamine Me ester, m. 128-9°, not convertible into the thiazolidine by ethereal HCl. The hippuryl analog similarly failed to cyclize in methanolic HCl. The desired "dehydropenicillin" was successfully synthesized from 2-carbethoxymethyl-4-carbomethoxy-5,5-dimethylthiazoline (XIV); this with **benzenediazonium** chloride gave the phenylazo deriv., m. 120°. V Me ester (3.2 g.) in 5 mL. CH₂(CO₂Et)₂ was added dropwise to 10 mL. C₂H(CO₂Et)₂ at 175°. After distn. in vacuo the residual oil was distd. at high vacuum, yielding 2.5 g. XIV, b0.018 156°, m. 109-11°. XIV (10.2 g.) in 75 mL. EtOH and 75 mL. 2N HCl was treated dropwise with stirring with 5.0 g. NaNO₂ in 20 mL. H₂O at 0°. After 15 min., the mixt. was dild. with H₂O to yield 2-isonitrosocarbethoxymethyl-4-carbomethoxy-5,5-dimethylthiazoline, m. 141°. Warming 0.4 g. of nitroso compd. in 8 mL. 2N NH₄OH for 5-10 min. on the steam bath with 1.2 g. Na₂S₂O₄ in 5 mL. H₂O gave 2-aminocarbethoxymethyl-4-carbomethoxy-5,5-dimethylthiazoline (XV).HCl, m. 163-7°. Phenylacetylation of 1.8 g. XV oxalate by stirring for 2.5 h. with 25 mL. Et₂O, 1.5 g. NaHCO₃, and 0.8 g. Ph₂CH₂COCl yielded 4-carbomethoxy-5,5-dimethyl-2-phenylacetamidocarbethoxymethylthiazoline (XVI), m. 136-7° (α-Et β-Me "benzyldehydropenicilloate"). Treatment of 0.6 g. XVI in 10 mL. EtOH with 3.06 mL. 0.51 N NaOH for 1 h. and acidification of the filtrate with 1 equiv. 0.5N HCl at 0° produced 4-carboxy-5,5-dimethyl-2-phenylacetamidocarbethoxymethylthiazoline, m. 120-4° (decompn.); morpholine salt, m. 173°, by preferential hydrolysis of the β-ester group. Refluxing 15 g. XVI gently with 220 mL. CHCl₃ and 8.5 g. PCl₅ 50 min., allowing to stand at room temp. several hrs., washing with aq. NaHCO₃, chromatographing over Al₂O₃, and recrystg. from CHCl₃-petr. ether yielded 7.5 g. "thiazolineoxazolone" (XVII, R = PhCH₂), m. 118-19°. The same compd. was produced from the corresponding α-benzyl β-Me ester (XVIII) by loss of the elements of PhCH₂OH. This remarkable formation of oxazolones rather than oxazoles by ring formation suggests that the precursors may have the structure RCONHC(CO₂R'):C.S.CMe₂.CH(CO₂R").NH, and yield by loss of the elements of R'OH compds. such as XVII. The p-nitrobenzamide analogs of XVII and XVIII and the corresponding compds. of the caproamido series were similarly prepd., providing the following compds.: 4-carbomethoxy-5,5-dimethyl-2-p-nitrobenzamidocarbethoxymethylthiazoline (XIX), m. 173°; 4-carboxy acid, m. 112°, remethylated to XIX. Shaking 4.23 g. XIX with 39.4 g. 0.51N NaOH 15 h., acidifying the filtrate at 0°, and purifn. through the Pb salt by decompn. with H₂S gave 4-carboxy-5,5-dimethyl-2-p-nitrobenzamidomethylthiazoline, m. 110° (softening). Refluxing 0.8 g. XIX in 15 mL. dry CHCl₃ with 1 g. PCl₅ 1 h. and chromatographing over Al₂O₃ yielded yellow prisms of 4-(4-carbomethoxy-5,5-dimethylthiazolin-2-yl)-5-ethoxy-2-(p-nitrophenyl)oxazole, m. 205°. Cyclization of XIX by

refluxing in CHCl_3 over PCl_5 , chromatographing the washed CHCl_3 soln. over Al_2O_3 , and recovering material from the upper part of the column gave XVII ($\text{R}=\text{p-O}_2\text{NC}_6\text{H}_4$) (XX), m. 265° . Caproylation of XV oxalate yielded 4-carbomethoxy-5,5-dimethyl-2-caproamidocarbethoxymethylthiazoline (XXI), m. $104-5^\circ$; 4-carboxy acid, m. $149-50^\circ$. Cyclization of XXI produced XVII ($\text{R} = \text{Am}$) (XXII), m. $87-8^\circ$. Heating 30 mL. $\text{NCCH}_2\text{CO}_2\text{Et}$ with 150 mL. PhCH_2OH at $194-200^\circ$ for 3 h. and removal of the residual PhCH_2OH at 100° and 18 min. yielded 34 g. $\text{NCCH}_2\text{CO}_2\text{CH}_2\text{Ph}$, b0.5 141° , $n_{\text{D}}^{19} 1.5206$. A mixt. of 17.5 g. ester and 4.6 g. anhyd. EtOH was treated with 3.8 g. dry HCl overnight, yielding 23.5 g. carbobenzyloxyacetimino Et ether-HCl, m. 89° (effervescence). Condensation of 5.1 g. HCl salt with 4.0 g. V Me ester, 2.5 g. AcOK, 5 mL. H_2O , and 5 mL. Et₂O by shaking together 2 h. yielded 3 g. 4-carbomethoxy-5,5-dimethyl-2-carbobenzyloxymethylthiazoline, m. 78° , converted to the oily 2-isonitroso deriv., reduced over HgAl in EtOH, and crystd. $\text{Me}_2\text{CO}-\text{Et}_2\text{O}$ in Et₂O to give 12.8 g. 4-carbomethoxy-5,5-dimethyl-2-aminocarbobenzyloxymethylthiazoline; oxalate (XXIII), m. $120-1^\circ$, phenylacetylated to XVIII, m. $132-3^\circ$; caproylated to the 2-caproamido deriv. (XXIV), m. 115° , and p-nitrobenzoylated to the 2-p-nitrobenzamido compd. (XXV), m. $182-3^\circ$. XVIII was sapond. to the 4-carboxy acid (XVIIIa), m. $153-4^\circ$. Cyclization of XVIII, XXIV, and XXV produced the "thiazoline-oxazolones" XXII, XX, and XVII. Cyclization of XVIIIa gave a "thiazoline-oxazolone" acid (XXVI), m. 190° (hemihydrate, m. $122-3^\circ$ (decompn.)); HCl salt, m. 165° (decompn.)) also obtained by hydrolysis of XVII. Methylation of XXVI with excess CH_2N_2 in ether gave the stereoisomeric N4-Me derivs. of the β -Me esters, m. $151-2^\circ$ and $110-111^\circ$. Many attempts were made without success to reduce XXV and the caproamido analog XXII and their Me esters to the penicillins or their esters. No appreciable biol. activity developed and vigorous redn. led by breakdown to unidentified products. In another procedure 13.3 g. PhCHClCOCl was added dropwise with cooling and stirring to 12 g. β,β -diethoxyalanine in 150 mL. N NaOH. After extn. with CHCl_3 , the aq. layer was acidified with 2N H_2SO_4 , the oily product was taken up in Et₂O, dried, and heated with excess CH_2N_2 in Et₂O. Distn. in high vacuum gave 12.6 g. pure Me α -chlorobenzylpenaldate di-Et acetal, m. $72-4^\circ$; 2,4-dinitrophenylhydrazone, m. $153-4^\circ$. Heating 3.3 g. acetal in 7 mL. glacial AcOH with 1.5 g. V.HCl. H_2O 30 min. and pptn. with 150 mL. dry Et₂O gave 2.83 g. α -Me DL-(α -chlorobenzyl)penicilloate-HCl, sintering at 95° , decomp. at 180° . Treatment of 10.52 g. HCl salt with 69.3 mL. N NaOH overnight and neutralization at 0° with 46.2 mL. N HCl yielded 5.2 g. DL-chlorobenzylpenicilloic acid, m. $85-90^\circ$ (decompn.), converted by shaking with 10.8 g. pyridine

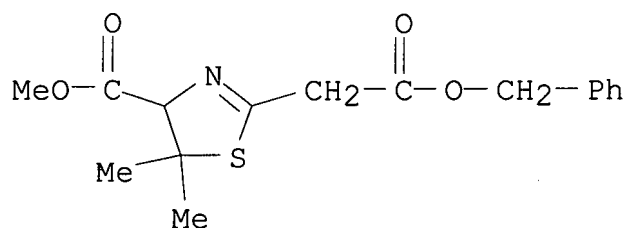
and 35.2 mL. Ac₂O to "benzyldehydropenicillin," m. 90-5° (decompn.), with the probable structure PhCH:C.O.CO.CMe:N.

All attempts at redn. failed. None of the expts. performed yielded penicillin. No active products were obtained from the action of phenylketene di-Me acetal on D-4-carbomethoxy-5,5-dimethyl- α -amino-2-thiazolidineacetic acid (XXVII) or of PhCCl₃ on the Na salt of XXVII in the presence of NaHCO₃, NEt₃, or pyridine. The reaction of COCl₂ with XXVII gave a bicyclic product (XXVIII), m. 168-9° (decompn.), [α]_D²³ 215° (EtOH), which was heated with PhCH₂MgCl in the hope that the Grignard product would undergo cyclization to penicillin Me ester. However, no activity was found in the reaction product. Since XXVIII was shown to have an active H atom, the use of MeCH₂CH:CHMgBr was later proposed (C.A. 39, 2968.2).

IT **875237-80-2**, 2-Thiazoline-2-acetic acid,
4-carboxy-5,5-dimethyl-, 2-benzyl 4-Me ester
(and isomer)

RN 875237-80-2 HCA

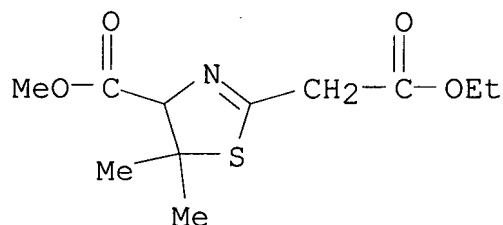
CN 2-Thiazoline-2-acetic acid, 4-carboxy-5,5-dimethyl-, 2-benzyl 4-Me ester (5CI) (CA INDEX NAME)



IT **721457-39-2P**, 2-Thiazoline-2-acetic acid,
4-carboxy-5,5-dimethyl-, 2-ethyl 4-methyl ester
(prepn. of)

RN 721457-39-2 HCA

CN 2-Thiazoline-2-acetic acid, 4-carboxy-5,5-dimethyl-, 2-ethyl 4-methyl ester (5CI) (CA INDEX NAME)



CC 10 (Organic Chemistry)

IT **875237-80-2**, 2-Thiazoline-2-acetic acid,

4-carboxy-5,5-dimethyl-, 2-benzyl 4-Me ester
(and isomer)